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EFFICIENCY OF WETTING AGENTS*

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INTRODUCTION

TEXTILE materials like raw cotton and wool, which are not uniformly and quickly wetted under normal circumstances, can be thoroughly wetted by the action of wetting agents which thus play a prominent part in processes like dyeing, finishing and kier-boiling in the textile industry Hundreds of wetting agents are now on the market and several new wetting agents are being discovered day to day The evaluation of a wetting agent has therefore become a matter of considerable practical importance

Several methods[1] are available for the determination of efficiency of wetting agents in industrial practice These methods however are semi-quantitative in character and only serve as a rough guide in textile practice. Theoretically, the determination of spreading coefficient of the wetting agent solution on the grey yarn should give a precise idea of the wetting power But the measurement of this quantity is beset with many difficulties since the system involves solids Complications due to roughness of the surface[6] and irreproducible kinetic effects and friction effects at the meniscus, render difficult to get at an accurate determination of the contact angles in such systems. For the evaluation of wetting agents, Cupples[5] worked out a method based on the fundamental similarity between the mineral oil surface and the hydrophobic portion of the inner surface of the grey yarn. His experimental procedure however is not satisfactory since he has measured surface tension by the ring method without taking necessary precautions.[7] Rao and Doss[8] have adopted the free lens technique of Langmuir for the purpose. The latter method is very cumbersome Rao and Doss have however shown that the surface tension lowering runs parallel to the wetting power In the present work this fact has been taken advantage of for comparing the efficiencies of some of the common wetting agents (pure and commercial) and for studying the effect of salts on the wetting efficiency. The surface

* Part of thesis submitted by T K. in partial fulfilment of the requirements for the degree of Master of Science in the University of Mysore.

tension lowering of five-minute-old surfaces has been determined by the ring method taking adequate precautions. A few measurements have also been made by the maximum bubble pressure method with a view to investigate the suitability of the method for the evaluation of wetting agents.

Experimental

The ring method.—The work was mainly on Nekal BX. Its purification has been described previously[8]. The other wetting agents used were commercial products and were used without purification.

For determining surface tension the ring method was employed. Temperature control was not aimed at, for, very precise measurements were not necessary since the aim of the work was only to classify the order of efficiency of the wetting agents. The solution under investigation was kept in a platinum dish. One advantage in using the dish was that the surface-active impurities in it could be completely removed by heating the dish to red heat before each experiment. In all the measurements the maximum pull for the five-minute-old surface was taken since it was not very convenient to measure the maximum pull more quickly. In every case the average of at least three values was taken as the representative value.

The maximum bubble pressure technique.—The technique introduced by Jæger was modified and used in this laboratory[10(a)] for the study of variation of surface tension of wetting agent solutions with time. This modified form of apparatus was employed in the present work. Air was pumped to the dropping tip through a constant head blow off, a drying tower, a buffer bottle and a capillary. The air was dried to prevent the condensation of the water vapour in the capillary tube and consequent blocking of the passage. The buffer bottle was used to check the pulsations in air. The dropping tip drawn out of a soft glass tube was washed with chromic acid mixture and distilled water. It was vertically fixed to the stand and could be moved up and down by means of a screw arrangement. The verticality was tested by viewing the tip and its reflection at a mercury surface The tips used required a pressure of about 15 and 13 cm. of xylene to force a bubble through water. The solution whose surface tension was to be measured was allowed to attain a temperature of $30° \pm 0.1°$ C, immersing the bottle containing the solution, in a water thermostat up to its neck and allowing it to remain there at least half an hour before the reading was taken. The bottle was then taken, opened and brought underneath the tip. The tip was then lowered slowly so that it just touched the surface of the liquid. A small length of the tip was then made to immerse under the solution by placing the container on a glass plate of known and uniform thickness. The pressure was adjusted

at the constant head blow off so that every bubble came out at an interval of five seconds. The maximum pressure was read out on the xylene manometer, employing a reading lens. The pressure, corrected for the height of the tip below the liquid, was proportional to the surface tension of the solution. Since the correction factor was practically equal to unity for a capillary of the size employed.[9] The correction to be applied for the pressure, shown by xylene manometer, for temperature fluctuations, was negligible and was always less than 0·1 per cent The apparatus was standardised by taking measurements both for water and toluene The results are noted in Table I, the surface tension of water being calculated on the basis of the standard value of the surface tension of toluene.

TABLE I

Liquid	Corrected maximum pressure	Calculated surface tension	Standard value of surface tension
Water ..	15·03 cm	71·11 dynes/cm	71 18 dynes/cm
Toluene ..	5·77 cm.	..	27·30 dynes/cm.

Preparation of the solutions —The stock solution was prepared by adding a calculated weight of the substance, and was stored in well cleaned jena bottles. Less concentrated solutions were obtained by progressive dilution on volume basis. The surface tension was measured soon after the solution was prepared. The solutions of commercial wetting agents were all prepared in 0·01 N acetate buffer of pH 3 7, so as to avoid the influence of varying pH on wetting efficiency Measurements were made with purified Nekal BX solutions with and without salts. The results obtained by the ring method are given in Tables II and III. The results obtained by the maximum bubble pressure method are given in Tables IV and V.

TABLE II

Surface tension of wetting agent solutions by the ring method

Age of the surface = 5′, pH 3 7; Temperature 28 ±2° C

Percentage of wetting agent	Nekal BX	Cardinol C A	Ultrawon WX.	Diazopon A	Igepon T	Surfax	Silvatol I	Turkey red oil	Triethanol amine
0·4	30·8	30·9	31·8	41 1	30 8	29·7	40 7	38·1	71·8
0·2	34·9	31·3	32·0	41 6	31·3	29·7	40 6	39·7	..
0·1	39·9	32 3	32·3	41·9	32·0	29 3	40 7	41·0	.
0·05	45·1	33 4	33·4	42·7	33 2	30 3	42·0	42·3	..
0·025	50·3	35·9	35·9	43·3	34·8	35 6	50·1	43·5	
0·01	..	..		.	39 1	45·5	.	45·3	.
0·005	..	..	..	..	45·0	..	.	47·2	..

TABLE III

Surface tension of purified Nekal BX solutions in water, acid and salt solutions Ring method

Age of surface = 5′ Temperature = 25° C ± 2° C

Percentage of Nekal BX	In Water	In 0 01 N HCl	In 0 01 N NaCl	In 0 1 N NaCl	In 0 01 N $BaCl_2$	In 0·01 N $BaCl_2$ + 1·25% Calgon	In 1·25% Calgon	Commercial Nekal BX solution in water
0 8	31·9	30 7	..	..		..	..	..
0 4	32 4	30·5	31·4	29 4		29·7	29·9	31 2
0·2	37 2	32·4	34 1	29 3		29·6	29 7	36 9
0 1	42 4	36 1	38 5	29 9		30·6	31·2	43 9
0·05	48 5	40 4	43 3	33 6		34 5	35·1	49 1
0·025	52 5	44 7	48 3	37·9	32 9	38 6	39 5	..
0·01	61 3	49 9	54 3	43 9	38 8	44 6	45 5	.
0·005	66 0	54·4	58 6	48 4	43 7	49 0	49 7	
0·0025	60 8	59 2	63 3	53 1	47·5	54 1	54 4	.
0·001		68 0	69 5	62 4	50·2	63·3	62 8	.
0 0005				70 0	.	69·7	69 7	..

TABLE IV

Surface tension of five-seconds'-old surface of Nekal BX solutions in 0 01 N hydrochloric acid by maximum bubble pressure method at 30° C.

Percentage concentration of Nekal BX	Surface tension in dynes per cm	
	Tip_1	Tip_2
0·8000	31·4	31·6
0·4000	31·7	33·0
0 2000	33 6	37·9
0·1000	38 9	.. ..
0·0500	45 7	54 1
0·0250	54·7	63·6
0·0100	64·2	68·0
0 0050	68 6	69·7
0 0025	69·9	70·1
0 0010	70 7	70·7

TABLE V

Surface tension of five-seconds'-old surface of commercial wetting agents of 1 0 per cent solutions in water by maximum bubble pressure method at 30° C

Name of the wetting agent	Surface tension in dynes per cm.	
	Tip_1	Tip_2
Surfax	29·80	30·1
Nekal BX	31·30	31·0
Gardinol C A	36·30	36·0
Igepon T	36·30	38·8
Turkey red oil	38·30	39·4
Silvatol I	40·00	39·8
Diazopon A	42·80	43 8
Ultrawon WX	47·60	49·8
Triethanolamine	71·30	71·1

DISCUSSION

1. *Relative efficiencies of some of the common wetting agents.*—A study of the variation of wetting efficiency of commercial Nekal BX solution with concentration by the apparent density method[11] has revealed that solutions

having concentrations higher than 0·2 per cent. have a high wetting power, while the wetting efficiency falls off quickly at lower concentrations. 0 2 per cent. solution of commercial Nekal BX in water was found to have a surface tension of about 36·9 dynes per cm. (*vide* Table III). It may therefore be assumed that the surface tension of any good wetting solution should be of the order of 37 dynes per cm. or less. Judged from this standard Diazopon A and Silvatol I are not sufficiently good wetting agents even at a concentration of 0 4 per cent. It may be pointed out in this connection that the former product is used mainly as an emulsifier and the latter is used as a detergent; thus, good detergent and emulsifying properties are not necessarily associated with good wetting action Turkey red oil also has a low wetting efficiency in acid medium. Triethanolamine has no wetting properties at all in acid medium. Gardinol C A., Ultrawon WX, Igepon T and Surfax are found to be very good wetting agents and indeed they are much better than Nekal BX. Igepon T is particularly good in that considerable wetting property persists even at low concentrations. These conclusions refer to media having a pH of 3·7

2. *Effect of salts.*—The influence of salts on the five-minute values of surface tension is interesting. An examination of Table III shows that barium chloride is much more effective than sodium chloride in reducing the surface tension This may be due to the Ba^{++} ions attaching themselves to the mono-layer reducing the electrical charge and consequently lowering the electrical potential barrier Hydrochloric acid itself is more effective than sodium chloride This can be correlated with the higher absorbability of hydrogen ions.[8] It is of interest to note that by the addition of sodium hexametaphosphate to the Nekal BX solution containing barium chloride, the influence of latter is largely annulled This is evidently due to the removal of Ba^{++} ions by the hexametaphosphate (Calgon) with the formation of soluble complex. Salts considerably increase the efficiency of wetting agents, though a salt by itself has no wetting power. In fact, the commercial sample (which contains sodium sulphate) has a higher efficiency than the pure sample itself at equivalent concentrations As has been already pointed out, divalent cations are much more effective than univalent ions in increasing the wetting power This fact is of special interest from the point of view of commercial practice. It is usual in the textile industry to soften the water before use But our results show that a small degree of hardness is highly beneficial to the action of the wetting agent. A similar effect has been observed by Kalinor.[8] It is important however not to have too high a concentration of the divalent cations since they may partially precipitate out the wetting agent and thereby reduce the wetting power,

3 *Maximum bubble pressure method.*—Though the maximum bubble pressure method has been used by Adam[4] for studying the variation of surface tension with time, it has been shown by S V Venkatachala[1(f)] that the method cannot be adopted for such studies since reproducible values cannot be obtained The irreproducibility is due to the fact that during the process of formation of the bubble large irregular changes in the area of the surface take place Venkatachala however observed that if the age of the surface was less than 5 seconds the values were fairly reproducible. The results got in the present work (Tables IV and V) show that with different tips the values of surface tension may sometimes differ by over 8 dynes per cm even when the age of the surface is 5 seconds This shows that the maximum bubble pressure method cannot be used for the measurement of surface tension of systems which exhibit a variation with time. A rough idea of the order of wetting efficiency of different solutions can however be obtained by this method.

Summary

The relative efficiencies of some of the common wetting agents have been determined by measuring the surface tension of five-minute-old surfaces of the solutions using the ring method in a modified form Aqueous solutions giving a surface tension of 37 dynes per cm may be considered to have good wetting properties It is found that wetting power is not necessarily associated with detergent and emulsifying properties.

Salts greatly increase wetting power Bivalent cations are more effective than univalent cations in increasing wetting power A moderate degree of hardness in water employed in preparing solutions of wetting agents may be of advantage in the textile industry

The maximum bubble pressure method is shown to be unsuitable for the measurement of surface tension of solutions which show a variation with time. A rough idea of the order of wetting efficiencies of wetting agents can however be obtained by measuring the surface tension of a five-second-old surface by this method.

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SPREADING OF CASEIN AND DERIVATIVES*

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During recent years there has been a great revival of interest in surface films, in particular those of proteins The surface behaviour of casein is of special interest since it can be studied both by the classical spreading method[4,5,6,9] and the new surface ageing technique developed by Doss[2] and independently by McBain and Wilson [18] In the present work the spreading of casein and some of its derivatives on aqueous substrates has been investigated.

Experimental

1 *Preparation of materials* —In some of the experiments casein (Hammersten) obtained from Kahlbaum was used Isodisperse casein obtained by the method of Svedberg, Carpenter and Carpenter[19] was also studied It was prepared as follows, Hammersten casein was extracted at 40° C for one hour with two litres of 70% ethyl alcohol containing one c.c of N hydrochloric acid per litre of alcohol The extract was centrifuged off from the residue. The soluble portion of the extract was reclaimed by precipitation with dilute sodium hydroxide and separated from the alcohol using the centrifuge. The solid was dried in a vacuum desiccator at laboratory temperature and dissolved in 0 2 N sodium acetate solution.

2 *Formolised casein* —0 05% solution of casein in 0 2 N sodium acetate was mixed with an equal volume of a 40% solution of formaldehyde. The mixture was allowed to stand for three days

3 *Deaminised casein* —Hammersten casein was deaminised according to the method of Dunn and Lewis [8] 140 c c of glacial acetic acid were added drop by drop, with vigorous stirring, to two litres of a 5% suspension of casein in water, the operation lasting two hours To the suspension, 500 c c of 8% sodium nitrite solution were added drop by drop for 1½ hours with vigorous stirring The mixture was allowed to stand for eighteen hours The precipitate of the deaminised protein was filtered, washed with hot water until free from nitrite and dried in a desiccator over concentrated

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* Part of thesis submitted by G N S in partial fulfilment of the requirements for the Degree of Master of Science of the Mysore University

sulphuric acid at the laboratory temperature The product was light yellow in colour but had a tendency to turn brown on exposure to light. It was therefore preserved in the dark. A portion of the product was dissolved in 0·5% sodium hydroxide The alkaline solution was deep red. The nitrogen content of the solid protein was determined by the Kjeldahl method and found to be 14 72% while the Hammersten casein had 15 43% This value corresponds to what was obtained by Dunn and Lewis [8]

4 *Sodium metaphosphate.*—This was prepared by heating sodium dihydrogen phosphate in a platinum dish for eight hours at redness. The red-hot dish was carefully quenched in water and the solid metaphosphate stored in a dry bottle

5. *Trichloracetic acid*—Acid of C P quality was used

The various buffer solutions were prepared from chemicals of C.P quality and the quinhydrone electrode was used to measure their pH

The Technique of Spreading and of the Measurement of Surface Pressure

The essential requirement for the quantitative study of protein films is a reliable and reproducible method for the preparation of films Since the proteins are soluble in water, there is always a risk of some of the protein entering into the bulk during the spreading process Several experimenters have described in detail the procedure to be followed for spreading in order to get reliable results Gorter and Grendel[6] forced the solution through a capillary kept horizontally and close to the surface Fourt and Schmidt[16] used a micrometer syringe and insisted on the needle being kept just above the surface and in contact with it Neurath[17] on the other hand, dropped the solution from a height of 2–3 mm from the surface and found that if the drops of the solution touched the surface before detaching themselves the spreading was incomplete Hughes and Rideal[10] spread gliadin by placing the solid protein on the surface and obtained more complete spreading than was got by Gorter's method The success in the former method is due to the fact that the capillary-active substances dissolved at a much slower rate, at the solid-water interface than at the contour in contact with the water-air interface This method, however, cannot be adopted with casein which does not spread in the solid form Langmuir and coworkers[11] spread the protein by taking its solution in the form of a band on a metal foil and slowly lowering the foil into the substrate This technique is elegant as it minimises the penetration of the spreading solution into the substrate in the process of dropping.

In our modification of the Langmuir method, two glass strips about 6" long and 1" wide were coated with paraffin, upto 2" from one end. The strips were handled at the paraffined ends only, thereby preventing the transfer of surface-active material from the hand to the exposed glass. The bare portions were cleaned in warm chromic acid and washed with water. A measured quantity of the protein solution was put on one of the strips and worked into a thin ribbon with the other strip. The strips were then slowly lowered into the surface

The surface pressure measurements were made by means of a film balance improvised from a Du Nouy tensiometer The trough was constructed of a beading of glass strips on a glass plate, using high grade paraffin from which traces of surface-active impurities had been removed by heating with activated silica gel Praffined glass strips were used as barriers Metal foils, coated with paraffin (in ether solution) prevented the leakage of the film to the other side of the float—a paraffined mica strip. Before each experiment the trough was always tested for contamination The entire apparatus was enclosed in a cabinet, with glass sides

Results

1. *Comparison of the two methods of spreading* —A comparative study was made of the direct dropping method and the modified band method. The results are given in Table I

Table I

A Spreading of casein (Hammersten) by dropping method on 0·01 N hydrochloric acid

Time allowed for spreading = 1 minute

Force in dynes per cm	Expt. 1 Area in sq metres per mg	Expt 2 Area in sq metres per mg.	Expt. 3 Area in sq metres per mg
1	0·70	0 71	0·68
2	0 62	0 61	0·60
3	0·57	0 55	0·55
4	0·55	0·53	0·52
5	0·53	0·50	0·51
6	0 50	0·48	0·49
7	0 48	0 46	0·47
8	0·46	0·44	0·45
9	0·44	0·42	0·43
10	0·42	0 40	0·41

Average limiting area = 0 61 sq. metres per mg.

B. Spreading of Hammersten casein by the modified band method on 0 01 N *hydrochloric acid*

Time allowed for spreading = 1 minute

orce in dynes er cm.	Expt 1 Area in sq. metres per mg.	Expt. 2 Area in sq metres per mg.	Expt 3 Area in sq. metres per mg
1	1·30	1·25	1·28
2	1·10	1·16	1·17
3	1 05	1 11	1·07
4	0·98	1 01	1·01
5	0·95	0·98	0·96
6	0 92	0·94	0 92
7	0·88	0·90	0·88
8	0 84	0·85	0·84
9	0·79	0 81	0 80
10	0·75	0·77	0·76

Average limiting area = 1 19 sq. metres per mg.

The results show that the modified band method is far superior to the dropping method Spreading by the former method is found to be quick, one minute being sufficient for complete spreading. The modified band method has therefore been employed in all subsequent work

Admixture with ethyl alcohol has been employed to enhance spreading.[14] The addition of alcohol to the spreading solution primarily helps by reducing the surface tension so that the liquid spreads more easily on water. Amyl alcohol, known to be more surface-active, can be expected to give better spreading of the protein. It has been tried by us, but contrary to expectation, the limiting area for casein was found to be only 0 47 sq metres per mg. The cause of this reduction in spreading is not clear. It is probably connected with denaturation, as can be gathered by the behaviour of denatured casein in the following experiment. Casein (Hammersten) was refluxed for an hour with absolute ethyl alcohol and dried for 2 hours at 80° The product was insoluble in warm 0·2 N sodium acetate and dissolved only in 0·5% alkali Spread from the alkali solution, the denatured casein was found to have on 0 01 N HCl substrate a limiting area of 0 84 sq. metres per mg. while before denaturation the corresponding value was 1·19.

2. *Effect of neutral salts on spreading of casein* —The influence of salts (in the substrate) on the spreading of casein was studied. The results are given in Table II.

TABLE II

pH	Substrate	Limiting area in sq metres per mg.
2·2	1 N Ammonium sulphate in 0·01 N HCl	1·16
2·2	1 N Potassium thiocyanate in 0·01 N HCl	1·19
5 9	0·5 N Barium chloride in distilled water	0·87
5·9	0·01 N ,, ,, ,, ,,	0·88
8 3	1 N ,, ,, 0·005 N borate buffer	0·99
8·3	0·05 N ,, ,, ,, ,,	0·90

The results indicate that salts have no appreciable effect on the spreading of casein on the acid side of the isoelectric point (pH 4 7). On the alkaline side, however, salts do increase the spreading

3 *Effect of pH on the spreading of casein* —The effect of pH on the spreading of the protein has been studied using different substrates The results are given in Table III

TABLE III

Time allowed in minutes	pH	Substrate	Limiting area in sq. metres per mg.
1	2·3	0 01 N Hydrochloric acid	1·16
30	2 3	0 01 N ,, ,,	1 19
1	1 2	0 1 N ,, ,,	1 22
1	4 7	0 005 N Acetate buffer	0 92
1	5 4	0 005 N ,, ,,	0 84
1	5 9	Distilled water	0 74
30	5 9	,, ,,	0·87
1	6 9	0 007 N Phosphate buffer	0·75
1	8 0	Sodium acetate + alkali	0·62
1	8 3	0 005 M Borate buffer	0·65

The results show that the limiting area diminishes with an increase in the pH There appears to be an ill-defined minimum in spreading at pH 8·0 It is of interest to note that casein does not attain maximum spreading at its isoeletric point Casein in this respect radically differs from egg albumin[8,15] and pepsin [7] Two factors seem to control the limiting area The extent of spreading itself, is controlled by the charge on the molecules in the film. This factor would lead to minimum spreading at the isoelectric point, for, the charge on the protein at this pH is minimum. At pH values far removed from the isoelectric point, the solubility of the protein is considerable so that the chances of the added liquid going into the bulk of the substrate (instead of spreading) are rendered greater. This factor by itself cause a maximum spreading at the isoelectric point At any pH

therefore one has to consider the effect due to both these factors. When the solubility effect becomes predominant there is maximum spreading at the isoelectric point. The increase in film areas on the highly acid side may be caused by the ionisation of the polar groups of film molecules Ionisation of the end groups brings into play repulsive forces between the molecules and enhances the spreading. With casein the solubility effect seems to be relatively unimportant in acid solutions, but the effect is prominent in neutral and alkaline solutions This explains why in the spreading of casein on an acid substrate, salts have no effect, while they have a marked effect in the case of a neutral or an alkaline substrate

4 *Effect of formaldehyde on the spreading of casein* —The spreading of solutions of casein treated with formaldehyde (for three days) has been studied The results are given in Table IV

TABLE IV

pH	Limiting area for the normal casein in sq metres per mg	Limiting area for the formolised casein
2 3	1 19	0 60
5 4	0 84	0 52
8·3	0 65	0 43

Formaldehyde therefore diminishes the spreading The influence of pH on spreading is also less. The decrease in spreading may be due to the formation of methyleneimino-compounds in which two molecules of the protein take part [1]

5 *Effect of sodium metaphosphate and of trichloracetic acid on spreading.*—These two reagents are known to coagulate proteins in solution. The effect of these two substances has therefore been studied The results are given in Tables V and VI.

A large reduction in spreading is noticed with the metaphosphate. It is known that metaphosphates form a complex between two amino groups. Complex formation is probably responsible for the lateral contraction of the film. Trichloracetic acid is without any effect on spreading. This may be correlated with the fact that 0 5% trichloracetic acid does not precipitate casein.

6. *Spreading of deaminised casein.*—The behaviour of deaminised casein is of great interest, as the film on dilute hydrochloric acid (pH 2 0, 3·0 and 4·0) collapses with time. At pH 2·2, the initial area of the film at a

TABLE V

Effect of metaphosphate

pH	% concentration of meta phosphate	Limiting area in sq. metres per mg.
1·2*	0·02	0 80
2·3*	0·02	0·79
2·3*	0·005	0 84
2·3*	0 0002	1 10
4·6 (Acetate buffer)	0 02	0·93

*pH was adjusted by adding hydrochloric acid.

TABLE VI

Effect of trichloracetic acid

H*	% concentration of trichloracetic acid	Limiting area in sq metres per mg.
2·3	0·5	1·19
2·3	0·05	1·18
2·3	0·005	1·19

*The pH was adjusted by adding the necessary quantity of HCl

pressure of one dyne per cm. is of the same order as that for Hammersten casein (13,000 sq. cm per mg) The limiting area however could not be determined as the film collapsed quickly at higher pressures. No film of deamınised casein could at all be got on distilled water.

7. *Spreading of isodisperse casein.*—Isodisperse casein prepared according to the method of Carpenter[13] is interesting since it has been shown to be a definite chemical individual with a molecular weight of 375,000. Table VII shows the behaviour of this protein on spreading.

TABLE VII

Time allowed for spreading = 1 minute

pH	Area in sq metres per mg.	Area per molecule in sq Å units
1·2	1·20	75,000
2·3	1 09	68,000
4·6	0·92	57,000
5·9	0·72	45,000
6·9	0·77	48,000

It is seen from Tables III and VII that isodisperse casein has the same spreading characteristics as the Hammersten casein.

SUMMARY

1. Casein has been spread from its aqueous solutions by different methods and it has been found that the modified band method is the most suitable for the study of protein films.

2 Effect of salts on the spreading of casein has been studied The results obtained can be explained on the basis that two different factors, solubility and the electric charge of the protein molecule influence spreading

3 Treatment of the protein with formaldehyde causes a decrease in spreading Change in pH affects spreading of formolised casein to a smaller degree.

4. Sodium metaphosphate diminishes markedly the spreading of casein Trichloracetic acid, however, has no effect

5. Deaminisation of casein alters the spreading properties and gives unstable films on acidulated water No films can be got on distilled water.

6. The spreading properties of an isodisperse fraction of casein have been studied The limiting area of this fraction has been found to be of the same order as that of the original material

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FLUORESCENCE REACTIONS WITH BORIC ACID AND *O*-HYDROXY-CARBONYL COMPOUNDS, AND THEIR APPLICATION IN ANALYTICAL CHEMISTRY

Part IV Azo-dyes from *o*-Hydroxy-carbonyl Compounds

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In the previous parts Neelakantam, *et al*[1] showed that solutions of many compounds containing the *o*-hydroxy-carbonyl group in concentrated sulphuric acid, when treated with boric acid, developed a marked fluorescence if originally non-fluorescent, or exhibited a marked intensification of the fluorescence already present This 'Fluorescence Effect' was noticeable in some cases in daylight but generally only under filtered U V light This remarkable behaviour was found to be quite characteristic of such molecules, and among the large number and wide variety of compounds already examined, there were only two exceptions which gave a positive reaction in the absence of this group It was also found that the introduction of the bathofloric bromine into the molecule of the compound did not lead to negative results in all cases It was, however, noted that while a positive reaction indicated the presence of the ortho-combination of the groups, the converse was not true With the introduction of the bathofloric nitro-group, the 'Fluorescence Effect' with boric acid also disappeared, while sulphonic group enhanced the effect

In the light of the previous work it is of considerable interest to investigate the effect of introducing the bathofloric azo-group, by coupling the *o*-hydroxy-carbonyl compounds with diazonium salts, on the Fluorescence Effect with boric acid Such an investigation was regarded of value for two reasons, *viz* .—(*a*) it would throw light on the scope of the test for detecting the group in molecules of such great tinctorial powers as the azo-dyes are; and (*b*) as a necessary extension of these investigations whose primary object was the development of suitable reagents for the detection and determination of boric acid In the course of investigations already reported, resacetophenone was found to give the best results in the test and was therefore suggested for the detection of micro-quantities of boric acid by a fluorescence reaction under filtered U.V. light [2] The utility of this reagent

is limited by the fact that the fluorescence in presence of boric acid is excited only under U.V. light. A reagent which yields similar results in daylight would indeed be very useful for the detection and should also prove of value for the determination of boric acid.

A large number and variety of azo-dyes can be prepared from aniline itself by diazotising and coupling with different *o*-hydroxy-carbonyl compounds, and by using other amines, an enormous number of compounds can be produced The present investigation, however, has been limited to seven of the commercial azo-dyes derived from salicylic acid, samples of which were available, and twenty azo-dyes which were synthesised for the purpose. Azo-dyes derived from salicylic acid have received special attention in this investigation for two reasons, *viz* :—(*a*) it is a typical *o*-hydroxy-carbonyl compound which is commonly available; and (*b*) it is specially characterised by a marked ability to fluoresce when compared with other compounds of the same group In strongly alkaline and concentrated solutions salicylic acid exhibits a deep violet fluorescence visible in daylight itself and very prominent under filtered U V. light In concentrated sulphuric acid solutions, the acid is non-fluorescent in daylight but strongly fluoresces in filtered U V. For purposes of comparison eight azo-dyes which contained one or more phenolic hydroxyls, but the *o*-hydroxy-carbonyl group was absent, were synthesised

TABLE I

No.	Azo-dye	Fluorescence (U V)		Remarks
		Blank	With boric acid	
1	Chrysamine G	Pale rose	Deeper	Pink solution ; deeper with boric acid, fluorescence difference quite prominent
2	Cotton yeollw, GI	Pale pink	,,	Pale brownish yellow solution ; pale orange with boric acid ; fluorescence difference quite prominent
3	,, R.	,,	,,	Pale reddish brown solution, yellowish brown with boric acid, fluorescence difference quite prominent
4	Diamine brown M	Nil	Nil	Pale blue solution, with boric acid pale violet
5	,, green B	,,	,,	Pale bluish violet solution, deeper with boric acid
6	Diamond black F	,,	Very pale green	Pale bluish green solution, with boric acid lighter in shade, fluorescence not marked
7	,, green B	Pale yellow	Deeper	Pale yellow solution ; with boric acid no change, fluorescence difference not marked

TABLE II

No.	Azo-dye		Colour	M P °C.	Fluorescence (U V)		Remarks
	Amine (diazotised)	Coupled with			Blank	With Boric acid	
1	Aniline	Resacetophenone	Reddish brown	198	Nil	Nil	Brownish yellow solution
2	,,	1-OH 2 Naphthoic acid	Chocolate	142	Pale skyblue	Pale skyblue	Bluish pink solution, with boric acid red tint increases
3	,	2-OH-3-Naphthoic acid	Deep red	206	Nil	Nil	Pink solution, with boric acid deeper
4	,	Salicylic acid	Brown	215	Pale yellow	Deeper	Yellow solution, no difference with boric acid
5	p-Nitraniline	,,	Brownish red	254	Nil	Nil	Pale orange solution, pure yellow with boric acid
6	m ,,		Brownish yellow	249	Very pale yellow	Deeper	Do fluorescence difference not prominent
7	α-Naphthylamine	,	Yellowish brown	212	Nil	Nil	Purple solution, with boric acid blue
8	β- ,,	,	Pale brown	236		,	Wine red solution, with boric acid slightly deeper
9	o-Aminophenol	,	Brownish yellow	152	Pale violet	Deeper	Solution colourless with and without boric acid; fluorescence difference very prominent
10	p- ,,	,,	Light orange	159	,,	,	,, ,,
11	Sulphanilic acid	,	Brownish yellow	,	Very pale yellow		Yellow solution, with boric acid no change, fluorescence difference not prominent
12	p-Chloraniline	,	Pale brown	248	Pale orange yellow	Pale orange yellow	No visible difference

13	m-Toluidine	"	Deep chocolate	210	Pale yellow	Deeper	Orange yellow solution; fluorescence difference not prominent
14	Anthranilic acid	"	Yellow	223	Very pale yellow	"	Pale orange solution; yellow with boric acid, fluorescence difference not prominent
15	Magenta	"	Chocolate	..	Pale yellow	Pale yellow	Blue solution (coupling with one mol salicylic acid); purplish with boric acid
16	"	"	Dark brown		Nil	Nil	Blue solution, purpled with boric acid (coupled with two molecules)
17	Chrysoidin	"	Chocolate brown	..	Very weak	Very weak	Brownish red solution, more red with boric acid
18	p-Amino-azobenzene	"	Dirty yellow	251	Pink	Deeper	Red solution, lighter with boric acid
19	Dinitro-diamino diphenylmethane	"	Reddish brown		Pale orange	Pale orange	Diazotised and coupled with one molecule of salicylic acid; brownish red solution; no colour change with boric acid, no difference in fluorescence
20	" "	"	Do.	..		"	Tetrazotised and coupled with two molecules of salicylic acid, brownish red solution, no colour change with boric acid

TABLE III

No	Azo-dye: Amine (diazotised)	Azo-dye: Coupled with	Colour	M P °C	Fluorescence (U V): Blank	Fluorescence (U V): With Boric acid	Remarks
1	Aniline	Phenol	Orange yellow	152	Nil	Nil	Brownish yellow, no change with boric acid
2	,,	*p*-Hydroxybenzoic acid	Brownish yellow	205	Nil	Nil	Brownish red solution, deeper with boric acid
3	,,	*m*- ,,	Khaki	210	Nil	Nil	Brownish yellow solution, no change with boric acid
4	,,	Resorcinol (Cerotine yellow R)	Orange red	155	Pale orange yellow	Pale orange yellow	No difference
5	,,	α-Naphthol	Deep chocolate	185	Nil	Nil	,,
6	,,	β- ,,	Orange red	131	Pale pink	Pale pink	,,
7	Sulphanilic acid	,, (orange II)	Orange	,,	Orange	Orange	Sodium salt, , deep pink solution. No change in colour or fluorescence with boric acid
8	*p*-Nitraniline	Resorcinol (Magneson)	Chocolate		Orange yellow	Orange yellow	Orange red solution, no change in colour or fluorescence with boric acid
9	,	β-Naphthol	Red	250	Nil	Nil	Deep pink solution, no change in colour or fluorescence with boric acid

Experimental

Azo-dyes.—The azo-dyes were prepared in the usual manner by diazotising the amine and adding the solution gradually to an alkaline solution of the coupling component The reaction mixture was kept distinctly alkaline and left over-night The solution was then acidified and heated to boiling. The precipitated dyes were filtered and crystallised generally from aqueous alcohol and in a few cases from water The dyes were characterised by their colour and melting points They generally sintered several degrees below the temperature at which they finally melted and it is the latter temperatures that are recorded in the table.

Fluorescence Test —The solutions were prepared and the tests carried out exactly as described in the previous communications When the solutions in sulphuric acid were strongly coloured, they were diluted until pale in colour.

As the source of U.V. a mercury are enclosed in a cabinet provided with an U.V.-filter which transmitted mostly in the U.V and a little in the violet-blue region was employed.

Results

The results are recorded in three tables given above, commercial samples in Table I and the prepared dyes in Table II Compounds included in both tables contain the *o*-hydroxy-carbonyl group For comparison, the results obtained with dyes in which this group is absent are given in Table III. With the exception of 'Magneson' (*p*-nitrobenzene-azo-resorcinol, B D H sample), the dyes included in the table were also prepared for this investigation.

Discussion

It is well known that while the azo-group is bathofloric, it does not destroy the ability to fluoresce completely, as does the nitro-group, but weakens. It can be seen from the data presented above, that several dyes of the azo-group fluoresce, though weakly, in concentrated sulphuric acid solution under ultra-violet light. On the addition of boric acid, however, the intensification of fluorescence does not occur in all cases, but there are several examples in which it does (*cf.* Tables I and II) A positive result in the fluorescence test appears to be independent of the ability of the parent molecule to fluoresce in solution and no generalisation with regard to the influence of substituents is at present possible It is, however, remarkable that though negative results have been recorded in the test with boric acid with several molecules which contained the *o*-hydroxy-carbonyl group, no positive result was obtained in the absence of this group as can be seen from Table III,

It is evident that the boric acid test for the *o*-hydroxy-carbonyl group is also applicable to the azo-compounds. However, negative results are obtained more often with the azo-dyes than with the *o*-hydroxy-carbonyl compounds from which they are derived. It may also be pointed out that the results are similar to those obtained with the brominated compounds already reported Thus it is clear that while a positive result confirms the *ortho*-orientation of the hydroxy and carbonyl groups, a negative result does not prove the contrary.

With regard to the second object of this investigation, it may be stated that only the *o*- and *p*-hydroxy-benzene-azo-salicylic acids gave fluorescence effects with boric acid approaching those with resacetophenone. These compounds do not possess any special advantages over resacetophenone as reagents for the detection of boric acid

Conclusion

The introduction of the azo-group into the molecule of an *o*-hydroxy-carbonyl compound does not invariably produce a negative result in the fluorescence test with boric acid carried out under filtered U.V. light. Fluorescence intensification on the addition of boric acid is observed in several cases, though there is a marked diminution in the intensity of the effect when compared with the parent *o*-hydroxy-carbonyl molecule.

The fluorescence test for the *ortho*-orientation of the hydroxyl and carbonyl groups is also applicable to the azo-dyes but a negative result does not prove the contrary.

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CONSTITUTION OF PATULETIN

Part II. A New Synthesis of the Flavonols of the Quercetagetin Series

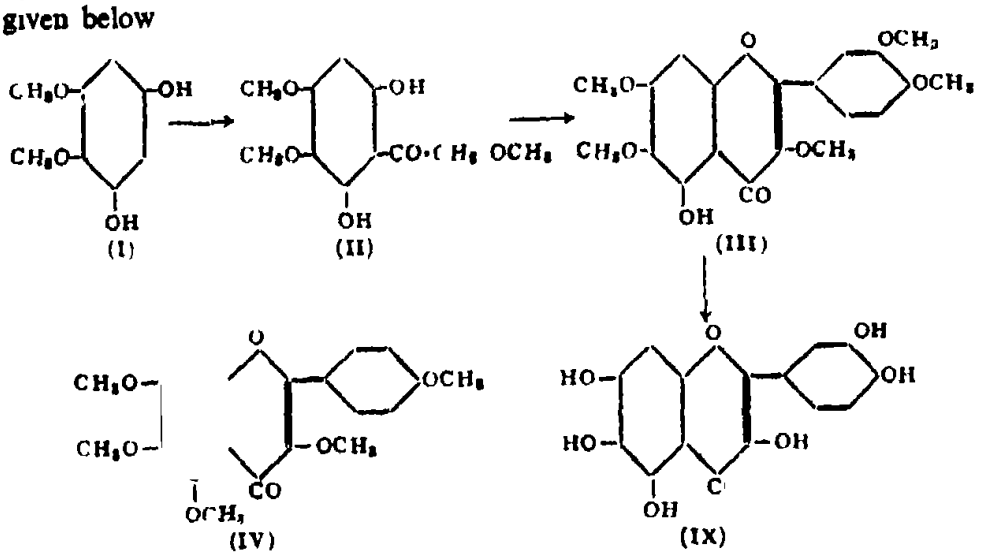
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Received October 27, 1945

From the experiments described in Part I[1] it could be surmised that patuletin is the 6-methyl ether of quercetagetin. Confirmation of this constitution appeared to depend on the discovery of a new method of synthesis of the flavonols of the quercetagetin series.

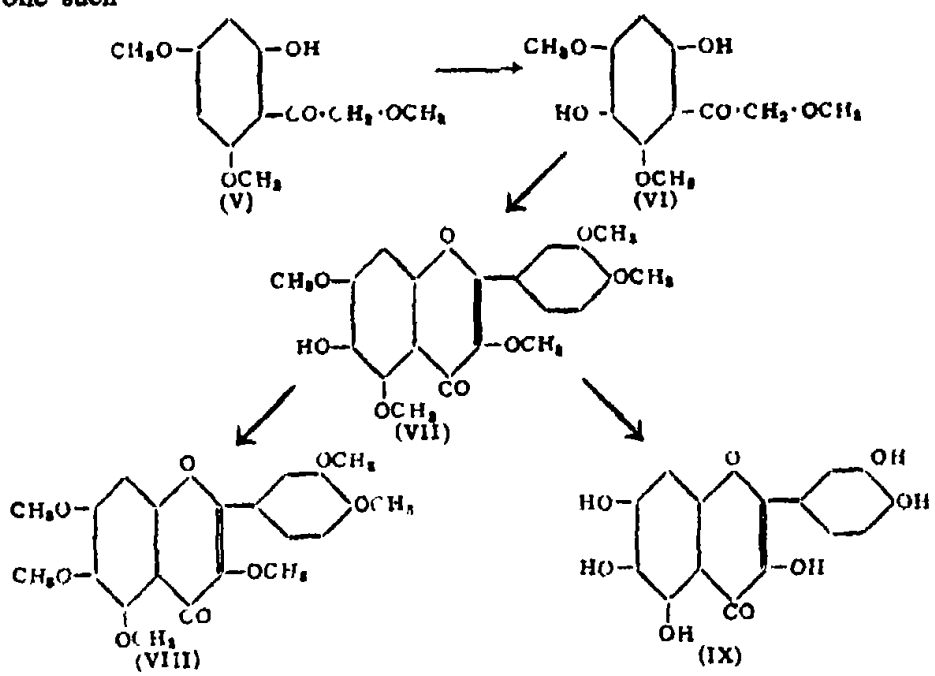
Two flavonols with the 5:6:7-arrangement of hydroxyl groups are known to occur in nature. The first is quercetagetin which is present partly free and partly as its glucoside, quercetagitrin, in the flowers of *Tagetes erecta*. The second is nor-tangeretin occurring as its pentamethyl ether, tangeretin, in the peels of *Tangerine oranges*. The former was synthesised by Baker, Nodzu and Robinson[2]. The main stages of their synthesis are given below:



When the ketone (II) is heated with a mixture of veratric anhydride and sodium veratrate, the pyrone ring may close in either of two ways, but the closure was found to take place exclusively in one manner yielding quercetagetin-pentamethyl ether. The other alternative would have resulted in the formation of gossypetin derivative but this did not happen

Tangeretin (IV) was obtained by Goldsworthy and Robinson[3] in a similar way using sodium anisate and anisic anhydride.

Though the above is an excellent method and works satisfactorily, it is not suitable for the present purpose It yields only 6:7-dimethoxy compounds, a 5·7 combination of methoxyls with the 6-hydroxyl free is desirable Further, the synthesis of 4:5-dimethoxy-resorcinol (I) starting from guaiacol is rather tedious as a large number of stages are involved. Consequently a different, and if possible, simpler scheme for the synthesis of quercetagetin and its analogues which may eventually lead to the establishment of the constitution of patuletin had to be sought The following is one such

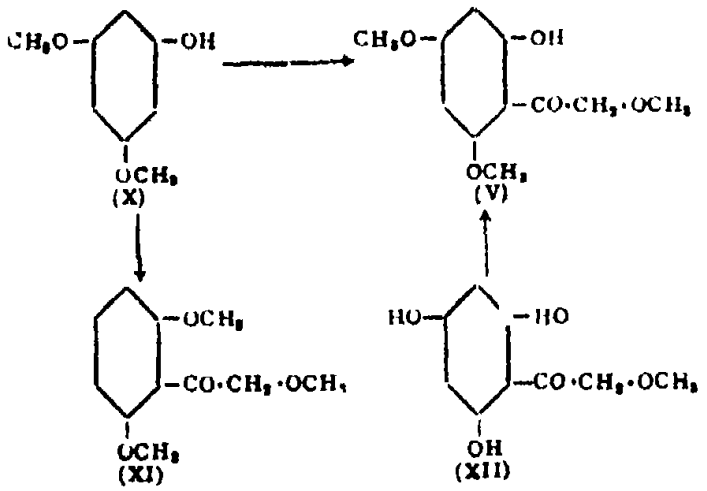


ω:4·6-Trimethoxy-phloroacetophenone (V) was obtained in the past by the alkaline degradation of the methyl ethers of flavonols[6] like quercetin but it does not seem to have been produced synthetically It has now been prepared by two methods. The first starts from the dimethyl ether of phloroglucinol (X) which is condensed with methoxy acetonitrile. Two products are possible and were actually isolated in equal amounts in the analogous case involving acetonitrile.[4] But here, ketone (V) is obtained as predominantly the main component. The mixture could be easily separated since the *para*-hydroxy isomer (XI) is soluble in aqueous sodium carbonate and the *ortho*-hydroxy compound (V) is not soluble in it.

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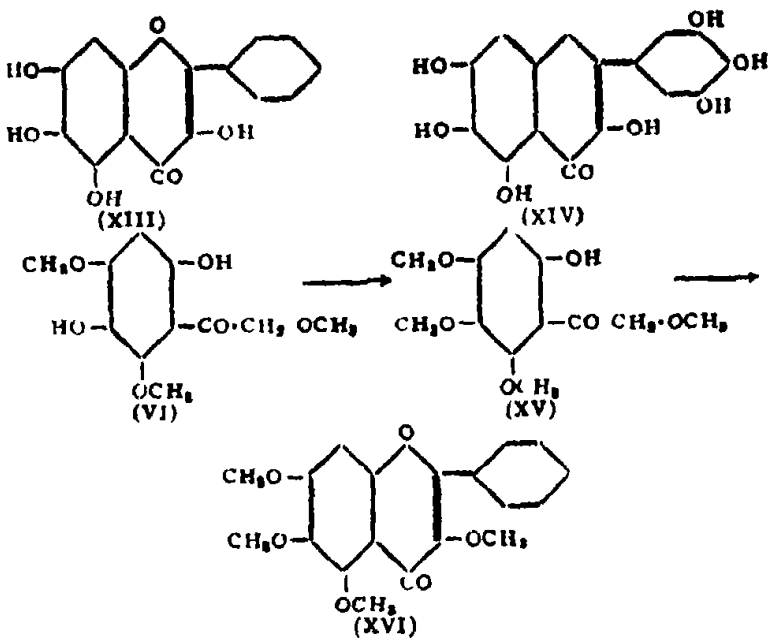
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The second method which is rather more convenient converts phloroglucinol directly into ω-methoxy-phloracetophenone (XII) which is then subjected to partial methylation with the required quantity of dimethyl sulphate and potassium carbonate in benzene-acetone solution to form the ω-4: 6-trimethyl ether (V)

Oxidation of the trimethyl ether (V) with alkaline potassium persulphate takes place fairly smoothly to yield the di-hydroxy compound (VI). The constitution of this product is not only based on well-established analogy but is also supported by its properties It does not give a precipitate with neutral lead acetate which is an indication that the hydroxy groups are not *ortho* to each other but *para*. A more definite support is its smooth conversion into quercetagetin-pentamethyl ether (VII) by fusion with veratric anhydride and sodium veratrate Further methylation of (VII) yields the hexamethyl ether (VIII) and demethylation yields quercetagetin (IX) both of which have been compared and found to be identical with authentic samples.[9] Thus the suitability of the proposed synthetic method has been established It is found to be quite convenient and easy to carry out and provides an intermediate compound with the 6-hydroxyl free

Using anisic anhydride and sodium anisate for condensation with the ketone (VI) and by subsequent methylation tangeretin[8] (IV) has been obtained. The method has also been applied for the synthesis of the two remaining members of this flavonol series which have not yet been discovered in nature but which probably occur in the plant kingdom; 6-hydroxy-galangin or 3: 5: 6: 7-tetrahydroxy-flavone (XIII) is the lowest member and 6-hydroxy-myricetin or 3: 5: 6: 7, 3′: 4′: 5′-hepta-hydroxy-flavone (XIV) is the highest.



It may also be mentioned here that the dihydroxy-ketone (VI) on careful partial methylation using one molecular proportion of dimethyl sulphate and potassium carbonate in benzene-acetone medium yields a tetra-methyl ether which is found to be identical with quercetagetol tetramethyl ether[8] (XV) obtained by the alkaline degradation of hexamethyl ether of quercetagetin (VIII). Thus this constitutes the first synthesis of quercetagetol tetramethyl ether. Its condensation with benzoic anhydride and sodium benzoate did not proceed smoothly and yield the expected 3 5·6·7-tetramethoxy flavone (XVI). The reaction seemed to be accompanied by some amount of demethylation of the 5-methoxyl group and the product was a mixture giving appreciable ferric chloride colour Further methylation, however, yielded a pure sample of the tetramethyl ether (XVI). It may be mentioned in this connection that in several experiments on the Allan and Robinson condensation of the ketone (VI), the products gave appreciable colour with ferric chloride, indicating slight demethylation, though this was not obvious from the analytical results In several other experiments, the products did not yield such colour with ferric chloride, and it could, therefore, be inferred that pure samples with 6-hydroxyl alone do not give this colour.

Experimental

ω: 4: 6-*Trimethoxy-2-hydroxyacetophenone (V)*:

(i) *Condensation of dimethyl ether of phloroglucinol with methoxyacetonitrile.*—Dimethyl ether of phloroglucinol (X) was prepared according

to the method of Pratt and Robinson.[5] The dimethyl ether (5·0 g.) was condensed with methoxy-acetonitrile (5 c.c) in anhydrous ether (50 c.c.) in presence of fused zinc chloride (1·0 g) by saturating the solution with dry hydrogen chloride at 0°. The ketimine hydrochlorides separated out on the sides of the flask even during the first hour After passing the current of hydrogen chloride for an hour after saturation, the flask was left in the refrigerator After three days, the ether was poured off and the mixture of ketimine hydrochlorides was washed with dry ether (50 c c)

A separation of the ketimine hydrochlorides depending on the different rates of hydrolysis was attempted but it was not successful The whole of the solid was treated with 50 c c of water, heated over a water-bath for a few minutes and quickly cooled No solid separated out. Therefore, more water (50 c c.) was added and the solution kept in a boiling water-bath for 45 minutes On cooling, a heavy oil separated out which did not solidify even after keeping for some hours in the ice-chest It was therefore extracted with ether A dark reddish brown resinous mass (0 8 g) was left behind being insoluble in ether This was rejected The ether layer was extracted thrice with aqueous sodium carbonate (5%)

On evaporating the ether layer, a light yellow oil was obtained which crystallised readily on scratching with a glass rod It was crystallised twice from alcohol when *ω*·4:6-trimethoxy-2-hydroxy-acetophenone (V) was obtained as colourless transparent prisms melting at 103–04° The melting point recorded in the literature[6] for hydroxy-fisetol-trimethyl ether is 102–04°. Yield, 1 8 g. [Found: C, 58·5; H, 6·3 $C_{11}H_{14}O_6$ requires C, 58 4; H, 6·2%.]

When the sodium carbonate extract was acidified a dark resinous mass was obtained in small yield. It was filtered and crystallised from alcohol containing acetic acid. On cooling, most of the resin came down as a dark amorphous powder which was filtered and rejected. From the filtrate by careful dilution with water a small quantity (0·1g) of the isomeric *ω*:2.6-trimethoxy-4-hydroxy-acetophenone (XI) was obtained It was crystallised once again from alcohol from which it came out as flat needles and rectangular plates melting at 259–60° It did not give any colour with ferric chloride in alcoholic solution. [Found C, 57 9, H, 6 3 $C_{11}H_{14}O_6$ requires C, 58·4 and H, 6·2%.]

(ii) *Partial methylation of ω-methoxy-phloroacetophenone (XII).*—*ω*-Methoxy-phloroacetophenone[7] (4 g) was dissolved in a mixture of anhydrous acetone (30 c.c) and anhydrous benzene (90 c c.) and the resulting solution was refluxed on a water-bath with freshly ignited potassium carbonate (10 g.)

and dimethyl sulphate (3·9 c c.). After refluxing for twelve hours the potassium salts were separated by filtration and washed thrice with warm benzene The filtrate was extracted with aqueous alkali (5%) four or five times On acidification, the alkali extract deposited the required ω: 4: 6-trimethoxy-2-hydroxy-acetophenone (V), the melting point being 98–100° C. When crystallised twice from alcohol, it was obtained as big colourless transparent prisms melting at 103–4° Yield, 2 75 g It dissolved in aqueous alkali yielding a pale yellow solution and with neutral ferric chloride a reddish brown colour was obtained in alcoholic solution

The potassium salts from a number of methylations were collected, dissolved in water and acidified with strong hydrochloric acid The turbid solution was extracted repeatedly with ether and the ether extract was shaken several times with sodium carbonate solution After separating the ether layer, the carbonate extract was acidified when a pale rose coloured solid (0·5 g.) was obtained. It crystallised from hot water in the form of colourless long prismatic rods melting at 208–10° [Found C, 56 7, H, 6 2, $C_{10}H_{12}O_6$ requires C, 56 6 and H, 5 7%] It gave a pink colour when treated with ferric chloride in alcoholic solution It was soluble in aqueous sodium hydroxide and sodium carbonate and was obviously a dimethyl ether. Its exact constitution is not yet determined.

ω-4. 6-Trimethoxy-2 5-dihydroxy-acetophenone (VI)

To a mechanically stirred solution of ω-4· 6-trimethoxy-2-hydroxy-acetophenone (V) (3 3 g.) in aqueous sodium hydroxide (50 c.c., 5%) kept at 15–20°, a solution of potassium persulphate (4 0 g. in 50 c.c. of water) was added slowly during the course of 3 hours The solution was allowed to stand for 20 hours and then rendered neutral to litmus with dilute hydrochloric acid. On stirring and scratching the sides of the container with a glass rod, the unreacted ketone (0·8 g.) separated out It was filtered off and the yellowish orange filtrate treated with concentrated hydrochloric acid (15 c c.). It was then heated on a steam-bath for 15 minutes and while still hot filtered through a bed of animal-charcoal under suction On cooling the clear orange coloured filtrate, it deposited a black resinous material which was separated by decanting the clear supernatant liquid. The required product slowly came out as shining bright yellow crystals when the decanted liquid was kept overnight in the ice-chest. It could also be extracted with ether. Repeated extraction with ether (six to eight times) was found necessary and in this case the yield of the oxidation product was better. It was crystallised twice from hot water using animal-charcoal, when it was obtained as bright yellow shining rhombohedral plates melting at 135–136°.

Yield, 0·8 g. [Found. C, 54·8; H, 6·0; $C_{11}H_{14}O_6$ requires C, 54·6 and H, 5 8%.] It dissolved in aqueous alkali forming a bright yellow solution which gradually turned orange-red In alcoholic solution a transient green colour was obtained with ferric chloride It did not give any precipitate with neutral lead acetate

ω-4·5:6-Tetramethoxy-2-hydroxy-acetophenone (Quercetagetol-tetramethyl-ether) (XV)·

A solution of dry ω·4·6-trimethoxy-2 5-dihydroxy-acetophenone (VI) (0·5 g) in anhydrous benzene (50 c c) was treated with dimethyl sulphate (0·25 g. in 5 c.c of benzene) and freshly ignited potassium carbonate (1 0 g) After refluxing on the water-bath for ten hours, the benzene solution was filtered and the potassium salts washed thrice with warm benzene (15 c c.) The benzene filtrate was repeatedly extracted with aqueous sodium hydroxide (5%) On acidifying the alkali layer with hydrochloric acid, the solution became turbid and did not deposit any crystals It was, therefore, left overnight in the refrigerator A pale red crystalline solid was deposited which was filtered, it crystallised from hot water as colourless long rectangular plates melting at 77–78° A second crystallisation from hot water did not raise the melting point Yield, 0 25 g It did not depress the melting point of the ketone obtained by the alkaline degradation of the hexamethyl ether of quercetagetin.[8] Both give the same brown colour reaction with ferric chloride in alcoholic solution. The synthetic product is therefore identical with quercetagetol-tetramethyl ether [Found C, 56 6, H, 6·6, $C_{13}H_{16}O_6$ requires C, 56 3 and H, 6·3]

The fully methylated ketone (pentamethyl ether) could be obtained as a pale yellow oil in a small quantity on evaporating the benzene layer But it was not further investigated

3·5 *7-Trimethoxy-6-hydroxy-flavone*.

An intimate mixture of ω 4·6-trimethoxy-2. 5-dihydroxy-acetophenone (VI) (1 0 g), benzoic anhydride (9 0 g.) and sodium benzoate (3 0 g) was heated under reduced pressure at 180–90° for five hours The mixture first fused and then solidified The crust was broken by means of a glass rod and refluxed with 30 c c of alcohol for 15 minutes The hot solution was then treated with alcoholic potash (30 c c containing 6 g. of potassium hydroxide) and the refluxing continued for 25 minutes more After removing the alcohol under reduced pressure, the dark brown residue was dissolved in water (150 c c.) and saturated with carbon dioxide A dark brown precipitate settled down. It was found advantageous to ether extract the solution

along with the precipitate instead of filtering, as the ether extracted only the desired flavone and not the accompanying resinous impurities. On removing the ether by evaporatation, the flavone separated out in the form of a pale yellow crystalline compound which was crystallised twice from alcohol. The 3·5.7-trimethoxy-6-hydroxy-flavone was obtained in the form of elongated rectangular prisms (rods) which sintered slightly at 162° and finally melted at 170° A third crystallisation was also done but there was no change in its behaviour on heating Yield, 0 4 g [Found. C, 66·0, H, 5 0; OCH_3, 27·3; $C_{18}H_{16}O_6$ requires C, 65 9; H, 4 9 and OCH_3, 28 3%]. In concentrated sulphuric acid, it dissolved yielding a pale yellow solution with no fluorescence.

3:5·6:7-*Tetra-methoxy-flavone* (*XVI*)·

First method.—A solution of 5 7.3-trimethoxy-6-hydroxy-flavone (0·1 g) in anhydrous acetone (30 c.c) was treated with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 0 g) and the mixture was refluxed for 12 hours The potassium salts were then removed by filtration and washed with warm acetone (15 c.c) On evaporating the acetone filtrate, a light reddish oily residue was left behind It was treated with dilute alcohol (3 c c 1 1) and left in the ice-chest overnight. A white crystalline compound separated out It was filtered and crystallised from ethyl acetate The tetramethyl ether was obtained as colourless flat needles and rectangular plates melting at 110–11° [Found C, 66 9, H, 5·7, $C_{19}H_{18}O_6$ requires C, 66 7, and H, 5 3%]

Second method—Quercetagetol-tetramethyl-ether (XV) (0 5 g) was condensed with benzoic anhydride (1 5 g) and sodium benzoate (0·5 g.) and the excess of the anhydride decomposed by heating with alcoholic potash (8%, 25 c.c.) When the alcohol was distilled off under reduced pressure and the residue treated with water a pale yellow crystalline powder was left undissolved It was filtered and washed with water and crystallised from alcohol Though it was crystalline in appearance it did not have a sharp melting point and it gave a greenish-brown colour with alcoholic ferric chloride Further crystallisation did not effect any improvement and the substance seemed to be a mixture arising probably out of partial demethylation in the 5-position during the Allan-Robinson condensation It was therefore methylated with dimethyl-sulphate and potassium carbonate in acetone medium. This product crystallised readily from ethyl acetate as colourless flat needles and was found to be identical with the tetramethoxy flavone described in the above experiment

3:5:6:7-*Tetrahydroxy-flavone* · 6-*hydroxy-galangin* (*XIII*):

The 3:5·7-trimethoxy-6-hydroxy-flavone (0·2 g.) was demethylated by refluxing a solution of the flavone in acetic anhydride (3 c c) with hydriodic acid (d 1 7, 5 c.c) for 2 hours The solution was then diluted to 25 c.c with water and saturated with sulphurdioxide when a pale orange-yellow precipitate separated out It was crystallised once from alcohol and twice from ethyl acetate, when the 5.6.7-trihydroxy-flavonol was otbained in the form of broken plates. It sintered at 240° and melted completely at 251–3°. Yield, 50 mg. [Found. C, 62 5, H, 3 9, $C_{18}H_{16}O_6$ requires C, 62·9 and H, 3·5%]

In alcoholic solution, the flavonol gave a dark olive green colour with ferric chloride. It did not exhibit any fluorescence either in alcoholic or sulphuric acid solution By acetylation with acetic anhydride and sodium acetate the acetyl derivative was prepared It crystallised from ethyl acetate in the form of spear-heads and melted at 186–88° with slight sintering at 182°

3.5:7:4′-*Tetramethoxy-6-hydroxy-flavone*

This compound was obtained by condensing ω·4:6-trimethoxy-2:5-dihydroxy-acetophenone (VI) (1 0 g) with anisic anhydride (12·0 g.) and sodium anisate (4 5 g.) After the hydrolysis of the condensation product, the alcohol was removed under reduced pressure and the residue dissolved in water. The dark brown solution was saturated with carbon dioxide and the liquid was extracted with ether exhaustively. On the removal of ether a pale yellow solid was obtained It crystallised from alcohol in the form of pale yellow prismatic rods melting between 195–98° A second crystallisation raised the melting point to 199–200°, with slight sintering at 195° Yield. 0·45 g. It dissolved in aqueous sodium hydroxide forming a pale yellow solution. With concentrated sulphuric acid it gave a yellow solution with no fluorescence [Found C, 63 7; H, 5 3, $C_{19}H_{18}O_7$ requires C, 63·7 and H, 5 0%.]

3:5:6:7:4′-*Penta-methoxy-flavone*. *Tangeretin* (*IV*)

The above tetramethoxy hydroxy-flavone (0·1 g) was methylated by refluxing it in anhydrous acetone solution (30 c c) with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (1 0 g.). After twelve hours, the solution was filtered off and the residue washed with warm acetone On evaporating the filtrate, a colourless crystalline material was obtained It crystallised from ethyl acetate in the form of rectangular plates melting at 153–54° (Goldsworthy and Robinson[8] also gave the melting point as

153–54°) It gave a blood red colour with concentrated nitric acid and a bright orange-yellow colour with concentrated hydrochloric acid. Yield· 65 mg [Found: C, 64 6, H, 5·7, $C_{20}H_{20}O_7$ requires C, 64·5; and H, 5·4%]

3.5 6:7·4'-*Pentahydroxy-flavone nor-tangeretin* ·

The above tetramethoxy-6-hydroxy-flavone (0·2 g.) was treated with hydriodic acid (d 1·7; 5 c.c.) in acetic anhydride (3 c c) and refluxed for an hour and a half There was separation of the orange-yellow hydriodide within an hour which caused bumping At the end of the reaction, the mixture was diluted with water and saturated with sulphur dioxide The pale yellow solid was collected and crystallised twice from dilute acetic acid The pentahydroxy-flavone was obtained as light yellow tiny rhombohedral prisms which darkened at about 275° and softened at 315–18°, but did not melt even at 325°.[3] Yield 0·1 g [Found C, 55 8; H, 4 0 $C_{15}H_{10}O_7$, H_2O requires C, 56·3 and H, 3 8%] Loss on drying *in vacuo* at 110–20°, 4·8%, $C_{15}H_{10}O_7$, H_2O requires loss on drying 5 0%. [Found in the sample dried at 110–20°: C, 59 5. H, 3 7, $C_{15}H_{10}O_7$ requires C, 59 6 and H, 3 3%.] In alcoholic solution, the flavonol gave a dark olive green colour with ferric chloride Lead acetate produced an orange precipitate which after some hours turned green On reduction with magnesium and hydrochloric acid a bright pinkish red solution was obtained

The acetyl derivative was prepared in the usual manner by boiling nor-tangeretin with acetic anhydride and freshly fused sodium acetate. On decomposing the excess of acetic anhydride by means of water, a colourless crystalline compound was obtained It showed a tendency to decompose when crystallised from alcohol It was therefore crystallised from ethyl acetate when it came out as thin broken plates melting at 234–35° [Found C, 58 2; H, 4 3; $C_{25}H_{26}O_{12}$ requires C, 58 6, and H, 3 9%.]

3·5.7.3'.4'-*Pentamethoxy-6-hydroxy-flavone* (*VII*)

ω:4:6-Trimethoxy-2 5-dihydroxy-acetophenone (VI) (1 0 g.) was condensed with veratric anhydride (10·3 g), and sodium veratrate (3·0 g.) and the brown product hydrolysed with alcoholic potash (80 c.c ; 10%) The residue obtained after removing the alcohol under reduced pressure, was dissolved in water and the solution saturated with carbon dioxide A dark brown solid was precipitated. It was filtered and when crystallised from acetic acid or alcohol only a brown amorphous substance could be obtained It was therefore rejected The filtrate was then extracted several times with ether From the ether extract a pale yellow crystalline solid was obtained on evaporation to dryness. The flavonol was crystallised twice from alcohol

when it came out in the form of lens-shaped crystals which sintered at 200°, and finally melted at 208–10°. A third crystallisation from the same solvent gave a bright yellow crystalline substance which melted at 209–10° with slight sintering at 200°. Yield. 0 46 g [Found C, 62 5, H, 5 5, $C_{20}H_{20}O_8$ requires C, 61 9 and H, 5 2%] The substance dissolved in alcohol and concentrated sulphuric acid yielding yellow solutions with no fluorescence

3 5·6:7·3′ 4′-*Hexamethoxy-flavone Hexamethyl-quercetagetin* (*VIII*) ·

This compound was obtained in the usual manner by methylating the 6-hydroxy compound (0·1 g,) obtained in the previous experiment in anhydrous acetone medium with dimethyl sulphate and anhydrous potassium carbonate It separated in the form of colourless shining crystals when the acetone solution was evaporated to dryness It was crystallised twice from alcohol and obtained as prismatic needles melting at 141–42° The mixed melting point with an authentic sample of hexamethyl-quercetagetin was not depressed [Found C, 62·7, , H, 5 6, $C_{21}H_{22}O_8$ requires C, 62 7 and H, 5 5%]

3 5:6·7·3′ 4′-*Hexahydroxy-flavone Quercetagetin* (*IX*)

It was obtained by demethylating the pentamethoxy-6-hydroxy-flavone with hydriodic acid (d 1 7) in the usual way On saturating the solution after dilution with sulphur dioxide, a pale yellow compound settled down It was crystallised first from alcohol and then from acetic acid The flavonol was now obtained in the form of short needles and plates melting at 315–18° and was found to be identical with quercetagetin [Found in air-dried sample C, 50 7, H, 4 3, $C_{15}H_{10}O_8$, $2H_2O$ requires C, 50 9 and H, 4 0]

On acetylation in the usual manner with acetic anhydride and sodium acetate, the acetyl derivative was obtained which on crystallisation from acetic acid appeared as long rectangular plates melting at 209–10° It was found to be identical with acetyl quercetagetin and it did not depress the melting point of an authentic sample

3 5 7 3′ 4′ 5′-*Hexamethoxy-6-hydroxy-flavone*

The condensation of ω 4 6-trimethoxy-2 5-dihydroxy-acetophenone (VI) (1 0 g.) with O-trimethyl-gallic anhydride (10 0 g) and sodium trimethyl gallate (3 0 g.) was made by heating the mixture at 180–185° under reduced pressure for 5 hours In the earlier stages of the condensation the mixture melted and there was considerable frothing which subsided after about three quarters of an hour At the end of the reaction the product was hydrolysed in the usual manner by refluxing with alcoholic potash (6 0 g in 60 c.c) for 20 minutes. The alcohol was removed under reduced pressure

and the product dissolved in water On saturating with carbon dioxide an appreciable quantity of dark amorphous resin separated out. It was rejected as it did not yield any crystalline material even after repeated crystallisations. The filtrate was extracted with ether repeatedly and from the ether extract, a yellow solid was obtained. It crystallised from alcohol in the form of golden yellow large square plates melting at 193–4°. It dissolved in aqueous alkali forming a pale yellow solution In concentrated sulphuric acid an orange-yellow solution was obtained which gave no fluorescence Yield, 0 45 g. [Found C, 60 5, H, 5 6, $C_{21}H_{22}O_9$ requires C, 60·3 and H, 5·3%]

3 5 6 7 3′ 4′ 5′-*Heptamethoxy-flavone* ·

Methylation of the flavonol (0·1 g) obtained in the above experiment was effected by means of dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone medium After refluxing the mixture for 12 hours, the acetone solution was separated by filtration and the residue on the filter washed with warm acetone On the removal of acetone by distillation, a brown semi-solid was obtained which deposited colourless crystals on adding a few drops of water When crystallised from alcohol it was obtained as flat needles melting at 150–51° [Found C, 61 6, H, 5 7, $C_{23}H_{24}O_9$ requires C, 61·1 and H, 5·6%]

3: 5· 6. 7 3′: 4′. 5′-*Hepta-hydroxy-flavone : 6-hydroxy-myricetin (XIV)*

The demethylation of the hexamethyl ether (0 3 g) was effected in the usual way by refluxing its solution in acetic anhydride with hydriodic acid (d, 1 7, 8 0 c c) on an oil-bath Within the first half hour, an orange-yellow crystalline solid separated out which caused occasional bumping After two hours, the solution was diluted and then saturated with sulphur dioxide. An orange residue was obtained which crystallised from acetic acid in the form of elongated narrow rectangular plates It did not melt below 325°, but darkened at about 315°. Yield. 0 1 g It was sparingly soluble in alcohol and acetic acid and gave a dark olive green colour with ferric chloride in alcoholic solution. In sodium hydroxide a yellow solution was obtained which rapidly changed to green and then to brownish yellow after some hours [Found in the oven dried sample· C, 54 3, H, 3 3; $C_{15}H_{10}O_9$ requires C, 53 9 and H, 3 0%]

On acetylation with acetic anhydride and sodium acetate, the acetyl derivative was obtained. When it was crystallised from ethyl acetate it came out in the form of stout rectangular prisms melting at 248–50°. [Found. C, 55 6; H, 4·2, $C_{30}H_{24}O_{16}$ requires C, 55 4 and H, 3·8%.].

Colour Reactions in Buffer Solutions

1. *6-Hydroxy-galangin* (*XIII*) (3. 5: 6: 7-*Tetrahydroxy-flavone*) ·

pH 8·6 Difficultly soluble; colour, pale yellow slowly changing to greenish yellow In the course of half-an-hour the solution was green After 24 hours, pale yellowish brown.

pH 9·8 Soluble more easily than in the previous case Bright yellow solution, within 5 minutes greenish yellow and green in 30 minutes After an hour bright green After 24 hours pale yellowish brown

pH 11·0 Same as above

pH 12·2 Immediately bright yellow, rapidly changed into green In a minute bright green. After 5 minutes green Afterwards the colour became paler After an hour, the solution was pure green and after 24 hours pale yellowish brown

pH 13 4 Bright yellow changing to green rapidly In a minute bright green After 5 minutes, bluish green slowly fading Within about half-an-hour it was pale green After 24 hours pale yellowish brown

2 *Nor-tangeretin* (3 5 6 7 4'-*pentahydroxy-flavone*) [3]

pH 8 6 Sparingly soluble, colour pale yellow turning green, within 15 minutes deep green Afterwards the colour began to fade with simultaneous development of brown colour After 24 hours, pale brown

pH 9 8 Rapidly went into solution with deep yellow colour turning within two minutes greenish yellow. Deep green after ten minutes and then began to fade After 24 hours pale brown

pH 11·0 Deep yellow, fast changing to greenish yellow. In a few minutes deep green After about ten minutes the colour began to fade while turning brown After an hour, brownish green After 24 hours pale brown

pH 12·2 Same as above but the colour changes were more rapid and within fifteen minutes the solution became almost colourless and did not change even after 24 hours

3 *6-Hydroxy-myricetin* (*XIV*) (3 5 6 7· 3' 4' 5'-*Hepta-hydroxy-flavone*).

pH 8 6 Bright yellow solution rapidly changing into green Within 2 minutes yellowish green After 5 minutes turning brown and 10 minutes yellowish brown No change after an hour After 24 hours, reddish brown.

pH 9 8 In the course of 5 minutes, the solution rapidly changed through greenish yellow to brown which did not change appreciably afterwards. After 24 hours, reddish brown

pH 11 0 Same as above.

pH 11 6 Same as above

pH 12 2 Deep yellow rapidly turning green and within a minute deep bluish green In another minute, violet brown. After five minutes it became brown After half-an-hour, reddish brown which practically remained unchanged even after 24 hours.

pH 12 8 Same as above without much difference

pH 13 4 Same as above but the solution did not become bluish green but changed rapidly in the course of a minute from yellow, through green to brown After 24 hours, it was reddish yellow

A similar study of quercetagetin has already been recorded.[9] The initial colour in all these cases is yellow turning to green as the most prominent colour which finally yields place to brown. With the increasing number of hydroxyls in the side-phenyl nucleus the green has a tendency to become deeper and assume a bluish tinge and the final colour changes from yellowish brown through brown to reddish brown The brown colour is most prominent in the highest member.

Summary

A new and convenient synthesis of the flavonols of the quercetagetin series is described ω 4 6-Trimethoxy-phloro-acetophenone has been prepared by two independent methods. By persulphate oxidation it is converted into the 2·5-dihydroxy compound Allan-Robinson condensation employing this ketone yields products containing a hydroxyl group in the 6-position Subsequent demethylation and methylation yields the flavonols and their fully methylated ethers. Besides quercetagetin and tangeretin which occur in nature, 6-hydroxy galangin and 6-hydroxy myricetin which have not yet been discovered in natural products, have also been synthesised.

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EXPERIMENTS ON THE RADIAL VARIATION OF CRITICAL VELOCITY OF WATER IN TUBES OF CIRCULAR CROSS-SECTION

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The present investigation was planned with a view of determining, if possible, at what point in the cross-section of a parallel tube through which water flows with stream-line motion, this motion first breaks down and becomes turbulent as the velocity is increased.

It was thought that this information might be of value as possibly affording some indication of the reason for the change from stream-line to turbulent motion at the critical velocity

The Apparatus

The apparatus used in the tests was a modification of that on which Osborne Reynolds carried out his classical experiments on critical velocities It consists of a large glass-sided tank 5-10½" long by 18" wide, fitted with baffles for steadying the flow from the inlet pipe, from which water was allowed to flow through a glass tube The rate of flow was regulated by a valve at the outlet from the tube The inlet end of the tube was fitted with a carefully finished bell mouthpiece

The motion in the tube was made visible by a colour band of aniline dye, supplied from a tank and discharged through a fine capillary tube at the entrance to the bell mouthpiece The position of this capillary tube could be regulated with precision both in a horizontal and a vertical direction by means of adjusting screens on its carrier.

At the point of observation of the coloured filament, the tube was enclosed in a glass-sided box, having vertical sides of parallel plate glass The box had an open top and was filled with water

In order to obtain the distance of the filament from the centre of the tube, a graduated scale was mounted on the vertical glass front of the box surrounding the tube, and a similar scale in the same plane across the open top of the box.

Above the box a plane mirror was mounted at 45° to the horizontal.

For observing the filament, two telescopes were mounted horizontally, one above the other, in the same vertical plane, *i.e.*, the plane containing the graduated scales. The upper one was focussed on the scale and on the filament, which was observed from above through the mirror, while the lower one was focussed on the filament as seen through the side of the box.

In this way the position of the filament at the section in question, with reference to each of the scales, and therefore with reference to the axis of the tube was obtained

In order to correct for refraction, a thin graduated scale was made to fit the internal diameter of the tube. This was inserted into the tube, which was filled with water as when carrying out an experiment, and the readings of the internal and external scales were compared over the whole radius. The experiments were carried out on tubes of four diameters, *viz.*, 0·5″; 1·0″; 1·25″; and 1·5″

Method of Carrying out Experiments

In carrying out an experiment the supply tank was filled and allowed to stand for some time in order to allow any initial disturbance of the water to die out. Some definite cross-section of the tube, at which to take observations, was then selected and the telescopes and gauges were brought into this plane. The outlet valve was then slightly opened and the rate of flow of the dye was regulated so as to give a fine colour band

The opening of the outlet valve was then gradually increased until a slight flicker of the colour band was noticed near the outlet end of the tube This indicates that the velocity was approaching the critical value.

A very slight increase in the velocity caused definite but intermittent breakdown into eddy formation at the end of the tube A further slight increase in the velocity caused the eddies to become permanent and brought the point of breakdown nearer to the tube entrance. In this way by adjusting the velocity the point of breakdown with the filament at any required radius, could be brought into the plane of observation

The exact radial position of the filament at this section was then observed and recorded, after which the mean velocity in the tube was determined by observing the time for the level in the supply tank to fall through a given distance when discharging under the same head with the inlet valve closed. The inverse of this time was proportional to the mean velocity of flow With

each tube the experiments were carried out for a series of radial positions of the filament, extending from the centre to a point near the walls.

Experimental Data

(1) *Experiments on tube* 1·5″ *diameter.*—This tube was 5 0′ long and the observations were made at a point distant 2·0 ft. from the inlet end.

The co-ordinates of the centre of the tube on the horizontal and vertical scale were·

Horizontal scale	4·38″
Vertical ,,	1·32″

The following table, which represents a typical set of observations, shows the horizontal and vertical co-ordinates of the filament at the instant of break-down, its radial distance from the centre of the tube, and the corresponding time for the level in the supply tank to fall through a distance of 1 inch.

Position of Colour Band		Distance from Centre	Time (Secs) for Level in Tank to fall 1 0″
Horizontal	Vertical		
4·38	1 33	01	42 5
4 20	1·38	1	44 0
4·25	1 32	230	48 2
4·15	1·49	265	51 2
4·24	1·06	295	52 2
4·63	1·04	38	58·5
3·00	1·34	38	58 0
4·00	1 35	39	59·1
4 11	1·65	·427	62·2
4·50	0·90	438	63·0
4·51	0·90	·44	63·2
4·00	1 10	·44	63 2
3·96	1·16	·45	64 0
4·81	1·40	50	66·0
4·02	1·70	53	62·8
3·88	1·52	·538	62·5
4·45	1·84	556	59·8
4·07	1 73	·515	66 0
3·80	1·32	·58	55 5
3 90	1·00	583	55·0
4 05	1·82	60	49·9
4·85	0 95	·632	45·0
4·01	1·83	·632	45·0

These times are plotted on a base showing the distance from the centre of the tube of the corresponding filament. From this it will be seen that as the distance of the filament from the centre of the tube increases, the velocity of flow necessary to produce break-down into turbulent motion

diminishes and attains a minimum value at a radius of approximately 0 5" after which it increases with a further increase in radius

This indicates that when, owing to increasing the velocity motion is made to break down at this section, the breakdown first occurs at a radius of approximately 0 475, or at a distance from the centre equal to 0·63 of the radius of the tube.

(2) *Experiments on tube* 1 25" *diameter.*—This tube was 4·33' long and the observations were made at a point distant 2 5' from the inlet end

The co-ordinates of the centre of the tube were.

Horizontal scale	.	2 48"
Vertical ,,	.	4·87"

The following table shows a set of experimental observations on the tube

Position of Colour Band		Distance from Centre Inches	Time from 12" to 11" (Secs)
Horiz Scale	Vert Scale		
2 49	4 91	04	62 8
2 47	4·80	07	64 2
2 50	4·78	092	55 6
2 60	4 71	20	57 0
2 50	4·62	25	61 2
2 48	4 62	25	60·2
2 49	4 56	31	75 0
2 49	4 51	36	87·2
2 47	4 48	39	86 2
2 49	4 44	43	79 0
2 49	4 42	·45	72 5
2·50	4 40	·47	62·6
2 48	4 30	57	75 0

As in the tests on the 1 5" tube, the velocity necessary to cause breakdown at this section diminishes with the distance of the filament from the centre of the tube and attains a minimum at a radius of 0 37" or 0·595 of the radius of the tube, afterwards increasing as the radius of the filament is increased

(3) *Experiments on tube* 1 0" *diameter.*—In order, if possible, to ensure that the position of the radius at which breakdown first occurs should not be affected by the stabilising effect of the bell-mouthed entrance to the tube, a larger tube—10' in length—was obtained for the second series of experiments This tube was 1·0" in diameter, and the observations were made at a section distant 5 0' or sixty pipe diameters from the inlet.

The co-ordinates of the centre of this tube were·

Horizontal scale	.	.	. 4·08″
Vertical ,,	.		1 66″

The following table shows a typical set of experimental observations on this tube.

Experiments on 1″ *tube, Length* 10′

Co-ordinates of Centre (1 66 4 08)

Position of Colour Band		Distance from Centre	Time (Secs) for Level in Tank to fall 1 0″
Vertical	Horizontal		
1 66	4 08	·0	75 6
1 73	4 10	071	79 0
1 56	4 08	10	80·1
1 59	4 00	106	82 3
1 70	3 94	146	86 1
1 60	3 89	·199	90·3
1·73	3 88	212	100 8
1 70	3 80	·282	108 1
1·70	3 75	331	112 7
1 90	3 77	388	108·0
1 68	3 69	395	90 7
1·63	3 68	·410	51 5

It will be seen that, as in the tests on the 1 5″ tube, the velocity necessary to cause breakdown at this section diminishes with the distance of the filament from the centre of the tube, and attains a minimum at a point whose radius (0 33″) is 0 66 of the radius of the tube, afterwards increasing with an increase in the radius.

(4) *Experiments on tube* 0 5″ *diameter* —This tube was 7 0′ long, and observations were made in this case at three sections, Section A was at a distance of 19″ from the entrance, Section B, 43″ from the entrance; and Section C, 72″ from the entrance

The experimental data are shown in the following tables

On comparing these, it appears that the radius of the tube at which the minimum velocity is required to cause breakdown is sensibly the same in each case, namely, 0 165′ or 0 66 of the radius of the tube.

The mean velocities required to cause this breakdown, however, diminish very appreciably with the distance from the entrance If the velocity required to breakdown at Section C be taken as unity, that at Section B is 1·17, and that at Section A is 1·91.

SECTION A

Distance 1'-7" from entrance

Centre co-ordinates (3·87 1·02)

Position of Colour Band		Distance from Centre	Time (Secs.) for Level in Tank to fall 1·0"
Horizontal	Vertical		
3·87	1 025	005	60·1
3 88	1 02	01	64·0
3·87	1 03	·01	63·6
3 87	1 07	05	69 0
3·81	1·02	·06	71 0
3 95	1·03	·081	78·0
4·00	1·02	·13	96·0
3 87	1 165	·145	103·5
4 01	1 09	·16	107·0
4 01	1·10	·166	109 4
3·88	1 20	180	75
3·74	1·16	189	94·1
4·09	1·02	22	75 1
4 07	1·16	·248	65·0

SECTION B

Centre co-ordinates (3·875 0·935)

Position of Colour Band		Distance from Centre	Time (Secs.) for Level in Tank to fall 1·0"
Horizontal	Vertical		
3·87	·96	·030	157 9
3·91	·93	·04	153 5
3 90	90	042	161·1
3·94	93	·070	159·0
3 90	1 00	076	153·8
3·84	1·04	114	171·2
3·99	93	·120	159·0
3·91	·80	·136	177·0
4 02	·93	·150	178·5
3·93	·78	·158	179·1
4·00	·83	·164	180·8
4 05	84	·175	179·4
4 03	1·03	·186	173·5
4·04	·83	·197	168·5
4·06	·950	·212	161 1
4·06	860	·22	157·5
4·06	·860	·22	155·0

This is due to the stabilising effect of the bell-mouth entrance, which is evidently still slightly felt at Section B which is 86 tube diameters from the entrance.

SECTION C

Taken at 6' from entrance

Centre co-ordinates (3·89 92)

Position of Colour Band		Distance from Centre	Time (Secs) for Level in Tank to fall 1 0"
Horizontal	Vertical		
3·90	92	01	194 5
3 90	933	016	195 8
3 91	933	024	196·1
3 89	95	03	194·0
3·89	1 00	·18	196·0
3·89	1·02	10	198 1
3 99	1·00	127	202·5
3 89	1 06	·140	200·8
3 99	1 05	15	205·1
4·04	99	·158	208·3
4 02	1 01	·166	210 3
4·01	1 06	·189	206·3
4 19	·92	·20	200 1

Careful measurements of the diameter of this 0·5" tube showed that it varies slightly, to the extent of 0 06" in its length of 7'. The experiments already described had been carried out with the smaller end at the entrance, and in order to determine the effect of this, the tube was reversed and the experiment repeated, observations being made at a point (Section D) corresponding to Section C, *i.e.*, 72 ins from the entrance.

The results of this experiment are shown in the following table.

SECTION D

(*Tube reversed*)

Taken at 6' from the entrance end

Centre co-ordinates (3·86 ·975)

Position of Colour Band		Distance from Centre	Time (Secs) for Level in Tank to fall 1 0"
Horizontal	Vertical		
0·97	3 86	·005	121·1
1·00	3 89	042	122 3
0·94	3·90	050	122 9
0·90	3·90	·080	125·0
0·97	3·95	090	127 3
1 03	3·93	·099	127 9
1·10	3·88	·133	136 1
1·03	3·98	136	137 0
1·05	3 98	·144	137·8
1·12	3·86	150	138 0
1·05	4·00	·161	139·1
1·13	3 93	·172	139·0
1·14	3·99	·214	133 1

The results show that while the radius of maximum instability is at the same point as before (at 0 66 of the radius of the tube) the velocity necessary to cause breakdown at this radius is 1 5 times as great as with flow in the opposite direction

Ratio of Velocities Required to Cause Breakdown of Motion at Centre and at Radius of Maximum Instability

From the various graphs, the ratio of the velocities required to cause breakdown of the motion at the radius of maximum instability and at the centre, can be obtained These are as follows

		Diam of tube "	Ratio
		1 5	0 65
		1 25	0 65
		1 0	0 70
		0 5	
Slightly divergent	.. 19" from entrance	.	0 56
	43 " "		0 88
	72 " " ..	.	0 92
Slightly convergent	72 " "		0 88

These figures show that this ratio is greatly affected by the proximity to the bell-mouthpiece On the whole, it would appear that the ratio increases slightly as the pipe diameter is decreased

Critical Velocity near the Wall of a Tube

In the experiments an observation very near the wall of the tube was found to be very difficult If the tube supplying the colour band was so adjusted that the colour band was very near the wall, it almost invariably touched the wall before observations could be made, and remained in contact with the wall

If, however, the curves be produced to a radius corresponding to that of the respective tubes, it appears that the velocity required to produce breakdown of motion near the wall is much greater than that required at any other point in the cross-section Taking the curves as a whole, it appears that the critical velocity is the same as at the centre, at a point whose radius is approximately 0 85 of the radius of the tube

Conclusions and Deductions

All the experiments indicate that when breakdown of motion initially streamline into turbulent motion occurs during flow through a tube, the

breakdown first occurs at a distance from the centre of the pipe, the experimental values ranging from 0 60 to 0 67 in the different tubes. From this point the turbulence spread inwards to the centre and outwards to the walls

The exact reason for the breakdown or the mechanism producing it is not as yet understood It is known to be due to the presence of the pipe walls, and to be independent of the roughness of the walls so long as the roughness is small It is not due to the attainment of a limiting shear stress in the fluid, since stream-line motion is possible in a small tube with shear stresses much greater than that obtaining at the critical velocity in a larger tube

An examination of the problem in the light of the experimental data of the present investigation, suggests that the breakdown may be related to the rate of variation of energy across a diameter of the tube Since the pressure across a section of a parallel tube in which the flow is stream-line is constant, the rate of variation of the energy per unit mass along a radius is the same as the rate of change of the kinetic energy and therefore of v^2

Assuming that some slight deviation of the particles from linear axial flow to be produced in any way, this will have its maximum disturbing effect if it occurs at a radius where the radial rate of change of energy is a maximum and therefore where $\frac{dv^2}{dr}$ is a maximum

But in stream-line flow through a tube of radius a,

$$v \propto (a^2 - r^2)$$

$$\frac{dv^2}{dr} \propto (a^2 - r^2)\, r$$

which is a maximum when $r = \frac{a}{\sqrt{3}} = 0\ 58\, a$

It is suggestive that this is very nearly the radius at which breakdown occurred in the experiments. The fact that the experimental value is somewhat greater than this is possibly due to the fact that in a tube whose walls are not perfectly smooth, those filaments nearest the walls suffer some slight lateral displacement due to the roughness, and thereby suffer a reduction in stability causing breakdown to occur somewhat nearer the walls than would be the case in an ideally smooth tube That this is a possible explanation is indicated by the fact that the radius of primary breakdown in the experiments was smallest in the two larger tubes, having a mean value of $0{\cdot}615\, a$ in these tubes, as compared with $0{\cdot}66\, a$ in the smaller tubes. As the surface

finish of all the tubes was as nearly as could be determined the same, the relative roughness would be smaller in the larger tubes.

It is to be noted that at the radius $(a/\sqrt{3})$, the value of $\frac{dv^2}{dr}$ is proportional to $a^2 \frac{dp}{dl}$ where $\frac{dp}{dl}$ is the pressure drop per unit length of the tube

But in the similar tubes the product $a\bar{v}$, where v is the mean velocity, is constant at the critical velocity, while $\frac{dp}{dl} \propto \frac{\bar{v}}{a^2}$ $\therefore a^2 \frac{dp}{dl}$ or $\frac{dv^2}{dr}$ is a constant at the critical velocity in tubes of different diameter

From this it would appear that in any tube the breakdown from streamline to turbulent motion, occurs when the gradient of energy along the radius exceeds a certain definite value, and that this factor is the criterion of such a breakdown

EFFECT OF SURFACE-ACTIVE AGENTS ON INDICATORS†

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Introduction

It is known that surface-active substances influence the determination of pH when carried out by the indicator method Smith and Jones[1] found that the presence of commercial wetting agents (Gardinol CA and Gardinol WA) often caused an error of more than one unit in pH when the common indicators are employed in the measurement. Hartley[2] made an extensive qualitative study of the phenomenon employing paraffin chain salts and found that the order of magnitude of the influence could be correlated with the valence change in indicators accompanying the colour change. In a recent paper, Hartley and Roe[3] have attempted to correlate the observed displacement of pH with the cataphoretic mobility of the micelles of the paraffin chain salts. The object of the present work is to study the effect quantitatively with a view to elucidate the phenomenon.

Experimental

The surface active substances used in the present work are Nekal BX (sodium di-alkyl naphthalene sulphonate) and Igepon T (sodium salt of oleyl-N-methyltaurine) Nekal BX was purified by the method described previouly.[4] Igepon T was purified by a similar method using ethyl alcohol as the solvent The product was dried in vacuum at 80° C. to 90° C. as it melted when dried at 100° C

The indicators employed were thymol blue and bromphenol blue supplied by the Hellige Company along with their comparator. 0·04 per cent. solutions were prepared by dissolving the solid indicators in the requisite quantity of alkali and making up with water[5]

The Hellige comparator was found to be unsuitable for the present work. Apart from the method being approximate (correct only to 0·2 unit) it was found impossible to match the colour of the test solution against any of the

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discs, when the wetting agent was present. For, the wetting agent is found to influence the light absorption characteristics of the indicators. The Hellige colorimeter was therefore employed for determining the ratio of the concentration of basic form to that of the acid form present in the test solution The apparent pH was calculated therefrom by means of the equation $pH = pK + \log \frac{(\text{basic form})}{(\text{acid form})}$ The standards used for such comparison always contained the wetting agent in the same concentration as in the test solution thus compensating for the change in the absorption characteristics By taking this precaution excellent matching could always be obtained. With bromphenol blue colour matching was not so good. The standards used were of the following composition.—

Standards for thymol blue—

Acid standard —The solution was made up from:

(*a*) 0·5 c c of the stock solution of the indicator
(*b*) 1 0 c c of 2 N hydrochloric acid solution
(*c*) Wetting agent in quantities to give the same concentration as in test solution. And
(*d*) Water to make up to 10 c.c

Basic standard :—

(*a*) 0·5 c c. of the stock solution of the indicator.
(*b*) Acetate buffer of pH 4 7 having sodium acetate concentration 0·2 N.
(*c*) Sufficient amount of wetting agent to give the same concentration as in test solution. And
(*d*) Water to make up to 10 c.c.

Standards for bromphenol blue—

Acid standard:—

(*a*) 0·5 c.c. of the stock solution of the indicator
(*b*) 1 c c of 2 N hydrochloric acid solution.
(*c*) Wetting agent in quantities to give the same concentration as in the test solution And
(*d*) Water to make up to 10 c c

Basic standard ·—

(*a*) 0·5 c.c of the stock solution of the indicator
(*b*) 5 c c. of N sodium acetate.
(*c*) Wetting agent in quantities to give the same concentration as in the test solution. And
(*d*) Water to make up to 10 c.c.

Test solutions were prepared as follows.—

(*a*) 0 5 c c of the stock solution of the indicator

(*b*) Sodium acetate and hydrochloric acid in quantities to give a pH in the working range of the indicator and ionic strength of either 0 1 or 0 01 as required.

(*c*) Wetting agent in quantities to get a required concentration

And (*d*) Water to make up to 10 c c.

The Sorenson values of the test solutions were determined by the quinhydrone method. The results obtained are given in Tables I to VIII

In measuring the apparent pH values the adjustments with the colorimeter could be made correct to about 0 03 unit in the sensitive range *The quinhydrone and the indicator methods gave slightly different values for buffered solutions and so an appropriate correction was applied in arriving at the* — ΔpH *values given in the tables*

TABLE I

Wetting agent Igepon T Indicator Thymol Blue Ionic strength of buffer = 0 01

g of wetting agent in 100 c c of the solution	Sorenson value (pH by quinhydrone electrode)	Apparent pH as shown by the indicator	Apparent shift in pH (− Δ pH)	$K_1 = 2 \cdot 8$, K_2 966 (− Δ pH theoretical)
1·000	3·24	1 10	2 13	2 41
0 500	3 07	0 97	2 09	2 31
0·200	2 94	0 83	2 10	2 10
0 100	2·88	0 96	1 91	1 88
0·050	2 86	1 10	1 75	1 64
0·020	2·83	1·30	1 52	1·26
0 010	2 83	1 80	1 02	1 02
0 005	2 83	2 17	0·65	0 76
0 000	2 83	2 82	0 00	0 00

TABLE II

Wetting agent Igepon T Indicator Thymol Blue Ionic strength of buffer = (

g of wetting agent in 100 c c. of the solution	Sorenson value (pH by quinhydrone electrode)	Apparent pH as shown by the indicator	Apparent shift in pH (− Δ pH)	$K_1 = 19 \cdot 1$, $K_2 = 706$ (− Δ pH theoretical)
1 000	2 97	1 37	1 59	1 55
0·500	2 90	1 33	1 50	1 52
0·350	2 84	1·33	1 44	1·51
0·200	2 84	1 30	1 47	1 47
0·150	2 84	1 35	1 42	1 44
0 100	2·84	1·40	1·37	1·39
0·050	2 84	1·46	1 31	1 27
0·020	2 84	1 68	1 09	1 04
0·010	2·84	1 94	0·83	0·83
0·005	2 84	2·09	0 69	0 69
0·000	2·83	2 76	0 00	0 00

Table III

Wetting agent Igepon T. Indicator Bromphenol Blue. Ionic strength of buffer = 0·01

				$K_2 = 6 \cdot 6$
2·00	4·54	3·21	1·41	1·52
1·00	4·41	3·61	0·88	0 88
0·50	4·41	3·82	0·67	0·63
0·25	4·41	3·86	0·68	0·53
0·20	4·39	4·04	0·43	0·37
0·10	4·39	4 22	0 25	0·29
0·05	4·37	4·28	0·17	0·13
0·00	4·36	4·44	0·00	0·00

Table IV

Wetting agent Igepon T Indicator Bromphenol Blue Ionic strength of buffer = 0·1.

p of wetting agent in 100 c. c. of the solution	Sorenson value (pH by quinhydrone electrode)	Apparent pH as shown by the indicator	Apparent shift in pH ($-\Delta$pH)	$K_2 = 21$ ($= \Delta$ pH theoretical)
2·00	4 70	3·35	1·51	1 63
1·00	4·70	3 52	1·34	1·34
0·50	4·70	3 80	1·06	1·06
0·20	4·71	4·13	0·74	0·72
0·10	4 71	4 30	0 57	0·49
0·05	4·73	4 43	0·46	0·32
0·00	4·78	4·89	0 00	0 00

Table V

Wetting agent · Nekal BX. Indicator Thymol Blue Ionic strength of buffer = 0·01

2·50	3·17	1·52	1 58
1·00	3 00	1·43	1·51
0·50	2·93	1·64	1·21
0·25	2·86	1 90	0·89
0·20	2·86	2·27	0·52
0·16	2 84	2·34	0·43
0·10	2·84	2·40	0·37
0·06	2·84	2·42	0·35
0·04	2·84	2·54	0·23
0·02	2·83	2 61	0 15
0·00	2·83	2·76	0 00

TABLE VI

Wetting agent Nekal BX. Indicator . Thymol Blue. Ionic strength of buffer = 0·1

g. of wetting agent in 100 c c of the solution	Sorenson value (pH by quinhydrone electrode)	Apparent pH as shown by the indicator	Apparent shift in pH ($-\Delta$ pH)
1·70	2·80	1·22	1·60
0·83	2·63	1 29	1·36
0·45	2·54	1 33	1 23
0·35	2 41	1·42	1 01
0·20	2·41	1 69	0·74
0 18	2 41	1 70	0·72
0 12	2 41	1·96	0 47
0·08	2 41	2·25	0·18
0·04	2·41	2·42	0 01
0·02	2 41	2·42	0 01
0 00	2 40	2 42	0 00

TABLE VII

Wetting agent Nekal BX Indicator Bromphenol Blue Ionic strength of buffer = 0·01

2 0	4 42	3·96	0 50
1·0	4·40	4·14	0 30
0 5	4·37	4 34	0·07
0 3	4 37	4·39	0 02
0·1	4·37	4 40	0·01
0·0	4·36	4 40	0 00

TABLE VIII

Wetting agent · Nekal BX Indicator Bromphenol Blue Ionic strength of buffer 0·1

2·00	4·68	4·20	0·61
1·00	4 70	4·34	0 49
0·50	4·71	4 65	0 19
0 30	4 71	4·77	0·07
0·20	4·71	4·80	0·04
0·10	4·71	4·84	0·00
0·05	4·71	4 85	0·00
0·00	4·71	4·84	0 00

DISCUSSION

1. *The mechanism of displacement of pH* —After making an extensive qualitative study of the effect of a few paraffin chain salts on a number of indicators, Hartley has suggested that the observed displacement of pH is due to the preferential adsorption of one of the forms of the dye on paraffin chain salt micelles. Indication of pH by a dye is dependent on the equilibrium between the two forms of the dye differing in valence. The equilibrium ratio of the two forms is determined by the pH of the solution. The acid form

of the dye is produced by the union between the basic form and the hydrogen ion. The valence of the acid form is therefore higher algebraically than the valence of the basic form The various possible types of valence for the two forms are.—

I. Both forms positively charged,
II. Acid form positively charged, basic form uncharged;
III Acid form uncharged, basic form negatively charged; And
IV. Both forms negatively charged

The surface active substances can also be divided into the different classes according to the charge possessed by their micelles in solution When an indicator is added to a solution containing a surface-active agent, there is a possibility that the micelles of the latter may preferentially adsorb one of the forms of the indicator Normally cationic micelle, however, would not take up any of the indicator of type I and anionic micelle would not adsorb any of the indicator of type IV owing to electrical repulsion; in these cases therefore, the surface-active substance would not affect the determination of pH This forms the basis of the sign rule of Hartley [2] In the other cases, there would be a preferential adsorption of one of the forms of the indicator Owing to the influence of the electric forces, the acid form which has a higher positive charge (or a lower negative charge) would be preferentially taken up by an anionic micelle The equilibrium between two forms would be consequently displaced, there being a shift towards the acid side. This results in the indication of lower pH A cationic micelle would behave in the opposite way causing an apparent increase in pH

In a later paper, Hartley has put forth another mechanism for explaining the displacement of pH brought about by paraffin chain salts when diphenylazo-*o*-nitrophenol is used as indicator In this case both the forms are almost completely adsorbed by the paraffin chain micelles. The micelle being negatively charged has in its immediate neighbourhood a high concentration of H^+ ions. The indicator therefore finds itself in a region of low pH. The pH indicated therefore is low and gives an idea of H^+ ion concentration near the surface of the micelles. Hartley has shown that there is an approximate correlation between the zeta potential of the micelle got from mobility measurements and that calculated from indicator experiments.

A complete picture of the phenomenon however can only be got by combining both the ideas put forth by Hartley and the following detailed mechanism is therefore proposed in the present paper The usual indicators are amphipathic substances having both a hydrophobic and hydrophilic portion in the molecule. The surface-active agents are also amphipathic

by nature When both these types of molecules are present in solution there is a tendency for complex formation The complex formation is brought about by the union of hydrophobic portion of the indicator with the hydrophobic portion of the molecules or micelles of the surface-active substances. The proportion of the acid and the basic forms of the indicator present in the complex would be controlled by (*a*) the local H^+ ion concentration near the indicator ion and (*b*) the relative life of the two types of the complexes Due to the difference in the electrical charge associated with the two forms of the indicator, one of the forms may produce a much stabler complex than the other. It is to be pointed out that both the factors act in the same direction in any particular system A careful study of these factors reveals that a quantitative formulation including these two factors is best done by applying the law of mass action on the basis of activities Since, however, the activity coefficients are not available for the complicated molecules or micelles dealt with in the present work it is simpler to formulate, employing the concentration terms, and discuss qualitatively the effect of the activity coefficients.

The quantitative aspect of the problem may now be considered In a solution containing the indicator and the surface-active agent, we have (1) the acid form of the indicator, H In (2) the basic form of the indicator In^- (3) the complex between the acid form of the indicator and the surface active ion H In. $.W^-$ And (4) the complex between the basic form of the indicator and the surface-active substance In^-. $.W^-$ These are in equilibrium. If activity coefficients are not taken into account and if the influence of micelle formation is assumed to be negligible, the following relationship can be formulated The theory would be applicable to the region wherein micelle formation does not set in or in cases where micelle formation would not effect the general behaviour of the system. Let the total concentration of the indicator be c, Let a fraction α be in the free basic form and a fraction β in the free acid form Applying the law of mass action to complex formation, we get

$$[In.. \quad W^-] = k_1 c_i \alpha \{cw - [In^- \qquad W^-]\}$$

where k_1 is a constant.

Similarly,

where k_2 is a constant. If x and y are the true and apparent pH values respectively, we get,

$$c_f a + \frac{k_1 c_f a c_w}{1 + k_1 c_w} =$$

and

$$1 +$$

Now,

$$k_1 c_f a = \frac{[\text{Wetting agent—basic form complex}]}{[\text{Free wetting agent}]}$$

and

$$k_2 c_f \beta = \frac{[\text{Wetting agent—acid form complex}]}{[\text{Free wetting agent}]}.$$

These quantities are small as compared with unity since only a small fraction of wetting agent forms the complex Thus, equation (1) gets reduced to,

$$-\Delta \text{ pH} = \log_{10} \frac{1 + k_2 c_w}{1 + k_1 c_w} \qquad (2)$$

2 *Thymol Blue-Igepon T system*—(i) The data obtained with the Igepon T-thymol blue system, are found to be in very good agreement with the above theory, as can be seen from Tables I and II Equation (2) has been used for calculating the theoretical values The values of k_1 and k_2 have been determined by making use of two of the experimental values of the pH shift

Apart from the fact that the experimental values can be fitted into the equation, it is to be pointed out that there are other interesting features in the experimental data to show that the theory adequately accounts for the experimental results —

Igepon T being a sulphonate gives a surface-active ion which is negatively charged The indicator thymol blue in the acid range has the basic form negatively charged and the acid form uncharged The acid form consequently gives rise to a stabler complex Moreover, owing to the Debye effect the negative surface-active ion induces a high local concentration of H^+ ions in the neighbourhood of the complex Thus the proportion of acid form in the complex would be very high. In equation 3 therefore k_1 would be much smaller than k_2 This is found to be the case.

(0 01 N buffer $k_1 = 2\ 8$, $k_2 = 968$,

0 1 N buffer $k_1 = 19$, $k_2 > = 706$)

(ii) At sufficiently high concentrations of the wetting agent, complex formation may be more or less complete, and consequently the pH shift would be practically independent of concentration This has been found to be the case

(iii) At low values for $k_1 c_w$, equation 3 becomes,

$$-\Delta \text{ pH} = \log_{10}(1 + k_2 c_w) \qquad (3)$$

It can be deduced from equation 3 that if a pH shift of 0·3 is produced by a certain concentration c_1 of the wetting agent (*a*) a shift of 1·0 unit would be produced by a concentration 9 c_1 and (*b*) a shift of 2 0 units would be brought about by a concentration 99 c_1 These conclusions hold within the limits of the experimental error in the experiments with 0 01 N buffer solutions With 0 1 N buffer solutions also the relation (*a*) is satisfied The relation (*b*) is not obeyed since $k_1 c_w$ becomes comparable with unity when c_w is equal to 99 c_1

3. *The bromphenol blue-Igepon T system* —It is known that the acid form of bromphenol blue has a single negative charge while the basic form has a double negative charge According to Hartley, there should be no shift in pH with this indicator, when a surface-active substance of the type of Igepon T (which has a surface-active anion) is added [2] Hartley based his conclusions on the idea that complexes between like charged molecules was improbable But, the experiments recorded in this paper show that there is a considerable displacement of pH in the present case This shows that in spite of the electrical repulsion between like charged molecules, complex formation between them does occur owing to the strong attractive forces between the hydrophobic portion of the wetting agent ion and that of the indicator ion. It may, however, be expected that complex formation would be relatively low, this would be especially true of the basic form which bears two negative charges One may therefore apply equation 3 which corresponds to the existence of the complex only with the acid form The calculated values of $-\Delta$pH on the basis of this equation and the corresponding experimental values are given in Tables III and IV. An examination of the tables shows that the experimental data support the theory. The other interesting features which support the thoery are:—

(*a*) The values of k_2 for bromphenol blue are much lower than the corresponding values for thymol blue showing that complex formation is much less in the former case. This is but to be expected since the acid form of the former indicator which forms the complex is negatively charged, whereas that of the latter indicator is uncharged.

(*b*) For the reason indicated above, the complex formation with bromphenol blue may be expected to be incomplete even at very high concentration of the wetting agent This is in agreement with the experimental data

(*c*) The conclusions drawn from equation 3 for thymol blue, also hold for bromphenol blue The concentration of wetting agent required to effect a shift of unity in pH is about 9 times the concentration required to cause a shift of 0·3 unit

(*d*) The shift in pH is found to be practically independent of indicator concentration

4 *Effect of ionic strength on the pH shift* —A comparison of tables I and II shows that an increase in ionic strength diminishes the pH shift in the case of thymol blue At lower concentrations of wetting agent, the effect of salts is small whereas it becomes considerable at high concentrations The effect can be quantitatively treated on lines similar to the treatment of neutral salt effect in reaction kinetics[6] The exact magnitude of the effect however cannot be calculated since the value of β in the equation, of Bronsted[6] is not known for the differennt molecules Due to the "α terms", however (which correspond to the zeta potential effect of Hartley) k_1 would increase whereas k_2 would be unaffected Experimentally this is found to be approximately the case. This explains, in fact, why at low concentrations of the wetting agent (where k_1 does not enter the equation), the effect of ionic strength is small It is of interest to note that k_2 does decrease to some extent with increase of ionic strength This decrease of the value of k_2 shows that the life of the complex from the acid form of the indicator is appreciably decreased by increase in the ionic strength. This is somewhat surprising since the acid form of thymol blue is known to be uncharged (from the simple theory of the neutral salt effect) and should not be affected by ionic strength It is to be noted however that the acid form of the indicator has a "Zwitterion" constitution and the observed effect only shows that the wetting agent ion is nearer to the positive charge of the "Zwitterion" than to the negative charge, this is but to be expected in view of the flexible nature of the hydrocarbon chain in Igepon T, which would help the orientation of its charged end to a position of minimum potential energy

At high concentrations of Igepon T where the complex formation is more or less complete, a change of ionic strength from 0·034 (in 1 per cent. solution of Igepon T in 0 01 N buffer) to 0·12 (in 1 per cent. solution of Igepon T in 0 1 N buffer), decreases the pH shift by about 0·6 unit. It is of interest to note that this corresponds very nearly to the effect of ionic

strength (c.a. 0·55 unit) observed by Hartley in the system investigated by him (indicator: diphenylazo-*o*-nitrophenol; surface-active substance: triethanol-ammonium cetane sulphonate) This shows that the changes in potential in the neighbourhood of the complex brought about by salts are almost the same in the two systems

A few experiments were tried with a view to get the maximum possible pH shift. It was possible to get as high a shift as 2·4 units by having the wetting agents at a concentration of 0·2 per cent in water and adjusting the pH to 4 2 (quinhydrone electrode) by adding acetic acid.

With bromphenol blue, increase in ionic strength *increases* the pH shift. This surprising feature is just the opposite of what has been observed in the present work with thymol blue and by Hartley and Roe with diphenylazo-o-nitrophenol. This effect can be explained as follows —As is already pointed out, the basic forms of the indicator which bears two negative charges, does not form any complex at all due to strong electrical repulsion. Increase of ionic strength no doubt decreases electrical repulsion; but the repulsion is yet too strong (at ionic strength = 0·1) for any complex formation Thus the basic form does not play any role in bringing about the observed effect For the same reason the observed pH changes are entirely determined by k_2 and follow equation (4) Complex formation of the acid form of the indicator however, is enhanced by the increase in ionic strength due to diminution in the electrical repulsion and thus causes the observed effect

5. *Nekal BX-Thymol Blue System* –An examination of the data in Tables 5 and 6 shows that the theory worked out for Igepon T is not applicable to the present system In the present case there is a certain concentration of the wetting agent at which the pH shift begins to increase considerably with concentration. This concentration value is 0·2 to 0 3 per cent. with 0·01 N buffer and 0·04 to 0 08 per cent with 0 1 N buffer. There is a striking coincidence between these values and the micelle formation concentrations got from surface tension studies[4] (*viz*, 0·07 per cent in 0·1 N buffer and 0 27 per cent in 0 01 N buffer) In this system the micelles appear to be much more effective than the single molecules in bringing about the pH shift. The complex formation is not as strong as with Igepon T since Nekal BX is relatively a short molecule and the electrical repulsion between the two negatively charged portions in the complex is consequently strong.

6. *Nekal BX-Bromphenol Blue System.*—The displacement of pH in the above system is very small This is to be expected for (*a*) Nekal BX is

a short molecule and hence electrical repulsive forces would be strong rendering the complex relatively unstable and (*b*) bromphenol blue having both the forms negatively charged would not be taken up by the wetting agent to any large extent Since the shift is very small, no discussion of the quantitative aspect is possible It may, however, be pointed out that the shift is marked, only at concentrations higher than at which micelle formation has occurred.

7. *Wetting power and pH shift.*—Since wetting action and the pH shift both involve the union of hydrophobic portions, it may be expected that there should be a general correlation between pH shift and wetting power An extensive investigation is desirable from this point of view The observations in the present work show that Igepon T is a much better wetting agent than Nekal BX, a conclusion which is also supported by surface tension studies[4].

SUMMARY

1. There is an apparent shift towards the acid side in the pH of buffered solutions as measured by the use of the indicators, thymol blue and bromphenol blue when wetting agents like Igepon T and Nekal BX are present in the system

2 Igepon T shows a very large shift with thymol blue. Under favourable conditions the shift may be as large as 2·4 units, an effect much bigger than what has been reported in literature so far for any system; Nekal BX shows less of the pH shift Both the wetting agents affect bromphenol blue to a smaller extent

3. A quantitative investigation of the phenomenon has been made A theory has been put forth, based on the formation of a complex between the wetting agent and the indicator to account quantitatively for the effect of concentration of the wetting agent on the pH shift.

4 Igepon T shows a marked shift with bromphenol blue as well This forms a clear exception to the sign rule of Hartley.

5 Increase in ionic strength decreases the pH shift with thymol blue as it is the case with the system worked by Hartley and Roe When bromphenol blue is used neutral salts produce an opposite effect An explanation is offered which account for these diverse results

6. The variation of pH shift with concentration of Nekal BX with thymol blue indicates that micelle formation of the wetting agent occurs rather suddenly.

7 The possible relationship between the pH shift and wetting power is pointed out

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CONSTITUTION OF KANUGIN—PART II

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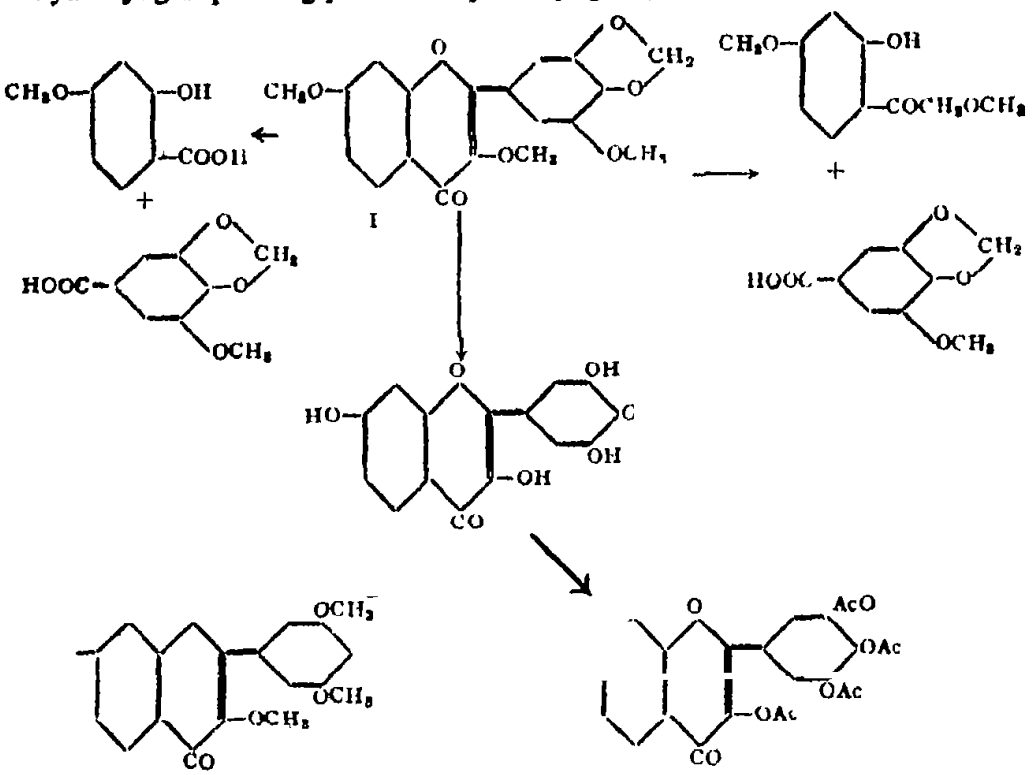
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In Part I[1] were described certain earlier experiments which could not be continued due to the war and the dislocation of our laboratories. It was, however, shown that kanugin is a flavone derivative giving the characteristic colour reactions and that it has a resorcinol unit since it yielded *p*-methoxy-salicylic acid on oxidation with permanganate or decomposition with alkali. The reaction with hydriodic acid could not be explained as simple demethylation since nor-kanugin did not regenerate kanugin on re-methylation but yielded a different substance Further work has now been possible and particulars regarding the complete constitution of kanugin are described in this paper.

Subsequent to our last publication it has been found that in the root bark of *Pongamia glabra* kanugin is accompanied by another related substance and careful and repeated crystallisation is necessary in order to remove it and obtain kanugin quite pure The second component seems to be more in abundance in thicker and more mature roots that have been used in later work. Consequent on this thorough purification, the melting point of kanugin has been raised to 203–05° and its analysis is found to agree more closely with the formula $C_{19}H_{16}O_7$. Further with concentrated sulphuric acid and a crystal of gallic acid it gives a bright green colour characteristic of a methylene-dioxy grouping.

Degradation with alkali has been investigated in detail. A repetition of the fission of kanugin with aqueous potash has yielded two acid products which could be separated by means of their marked difference in solubility in water. The less soluble one is identified as myristicic acid by analysis, colour reaction, and by comparison with an authentic sample prepared starting from oil of nutmeg. The more soluble portion is found to be the same as the impure form of *p*-methoxy-salicylic acid mentioned in Part I. This identification has been confirmed by the convertion of the product into the 5-bromo-derivative and subsequent esterification to form the methyl ester of 5-bromo-4-methoxy-salicylic acid These derivatives could be easily obtained pure since they are sparingly soluble, and they are found to be identical with authentic samples prepared from synthetic 4-methoxy-salicylic acid.

Degradation using absolute alcoholic potash has gone much better and yielded myristicic acid and ω: 4-dimethoxy-2-hydroxy-acetophenone in good yields. From these results it is clear that kanugin is a robinetin derivative and that it has a methylenedioxy group in the 3'·4'-positions, the other three hydroxyl groups being protected by methyl groups (I)



The above constitution explains the peculiar results obtained by the treatment of kanugin with hydriodic acid and the re-methylation of nor-kanugin.

When purified kanugin is employed, the nor-kanugin obtained has slightly different properties from those already recorded. It is a yellow crystalline substance melting at about 325° with decomposition and its composition corresponds with the formula $C_{15}H_{10}O_7$. Its pentamethyl ether melts at 148–49° and its penta-acetate at 223–25°. Its identity with robinetin has been established by comparison with a synthetic sample obtained by the method of Allan and Robinson, starting from ω-methoxy resacetophenone and the sodium salt and anhydride of *O*-trimethyl gallic acid, followed by demethylation.[8] Mixed melting point determinations of the flavonols and their derivatives have been made as also a comparison of the colour reactions of the two samples under identical conditions. The data are presented in the following table.

Property	Nor kanugin	Robinetin
1. Melting point of the flavonol	320–25°	320–25°
2. Colour with $FeCl_3$	Dark olive brown	Dark olive brown
3 Precipitate with lead acetate	Red	Red
4 Colour changes at pH 11	Quickly dissolves to a yellow solution, changes to emerald green in 10 seconds, then to greenish blue and pure blue, changes further to violet and finally pink, resembling alkaline phenolphthalein This colour is stable for an hour and fades to brown through brown pink	
5. Melting point of the methyl ether	135–36° and 148–49°	135–36° and 148–49°
6 Melting point of the acetate	223–25°	223–25°

Some samples of the pentamethyl ether of nor-kanugin (natural) and of robinetin (synthetic) have been found to be melting at 148–49° and some others at 135–36° But in the latter case, when the melt is allowed to solidify, the solid subsequently melts at 148° A mixture of the low and high melting samples melts only at 148° It may therefore be concluded that there are two forms of the solid methyl ether having two different melting points

In the constitution of kanugin given above, two important features should be noted Kanugin belongs to the small number of naturally occurring anthoxanthin derivatives in which all the hydroxyl groups are protected. But the more important point is the use of a methylene group for this protection, this being the first instance where this group has been found in the flavone series

It may be interesting to compare the crystalline flavonol components present in the different parts of the Pongamia tree The seeds[3] contain karanjin which may be considered to be a derivative of 3, 7-dihydroxy-flavone, *ie*, derived from resorcinol The constitution of the other crystalline substance pongamol, also present in the seeds, is not yet clearly known. Kæmpferol is found in the flowers[4] It is also a flavonol but is derived from phloroglucinol The constitution of pongamin which is found in very small amounts in the flowers is still unknown The root bark[5] contains kanugin which is again a flavonol derived from resorcinol but the side-phenyl nucleus is in a higher state of oxidation Another noteworthy feature is that in the flowers the protection of the hydroxyl groups is the least whereas in the roots it is complete; an efficient mechanism should therefore be available in this part of the plant for this protection

Experimental

Kanugin

The sample of kanugin obtained from the root bark of *Pongamia glabra* was crystallised using excess of alcohol in which it is sparingly soluble. The

light colourless crystalline solid that was produced after two crystallisations melted between 196 and 200° For further purification it was again crystallised twice using a mixture of alcohol and acetic acid. It then came out as colourless brittle rectangular plates and needles with a pearly lustre melting at 203–05° Further crystallisation did not raise the melting point [Found: C, 63·8; H, 4·7; OCH_3, 25·8; $C_{18}H_{16}O_7$ requires C, 64·0; H, 4·5; OCH_3 (3), 26·1%]. It dissolved in concentrated sulphuric acid to give a bright yellow solution and the colour changes and fluorescence were exhibited as reported previously Even an alcoholic solution gave a blue-violet fluorescence; with magnesium and hydrochloric acid a brilliant scarlet red colour was produced When gently warmed with a solution of gallic acid in concentrated sulphuric acid, a deep emerald green colour was obtained in 10 seconds

Alkaline Hydrolysis of Kanugin

(1) ***Using aqueous alcoholic potash*** —Kanugin (0 5 g) was dissolved in aqueous alcoholic potash (alcohol 40 c.c , water 40 c c. and potash 5 g) and the solution boiled under reflux for 6 hours in an atmosphere of hydrogen. It was then cooled, acidified with hydrochloric acid and the alcohol distilled off under reduced pressure The residue was then extracted repeatedly with ether The ether solution was then shaken first with aqueous sodium bicarbonate in order to separate acid products (A) and subsequently with dilute sodium hydroxide to remove phenolic components (B) Neutral products would then be left in the ether solution (C) (B) and (C) were found to be insignificant in amount and were not further studied.

On acidifying the bicarbonate extract a solid separated out. This was washed with water and marked (D) By ether-extracting the solution the more soluble part was isolated (E). When (D) was crystallised from dilute alcohol it melted at 212–13° and had the appearance of long rectangular plates and prisms with a tendency to taper at the ends (Found: C, 55·3; H, 4·4; OCH_3, 16 3; $C_9H_8O_4$ requires C, 55 1; H, 4 1 and OCH_3, 15·8%). It formed a yellow solution in concentrated sulphuric acid; when a crystal of gallic acid was added and the solution gently warmed the colour changed to bright emerald green and finally to a stable pure blue The mixed melting point with an authentic sample of myristicic acid prepared from oil of nutmeg was not depressed

When (E) was crystallised from boiling water it yielded a colourless crystalline product (flat needles) which had an indefinite melting point (130–45°), gave a purple colour with ferric chloride and had all the properties of a similar sample (4-methoxy-salicylic acid) already reported in Part I.

The substance (0·2 g) was dissolved in glacial acetic acid (3 c c.) and treated with a slight excess of a solution of bromine in acetic acid. The solution was rapidly decolourised and on keeping the mixture for a few hours at 0° a crystalline solid separated out It was filtered and washed with a little water. Since it was very sparingly soluble in solvents it was purified by boiling with glacial acetic acid It then melted at 258–59° with sintering a little earlier and had the appearance of small rectangular plates (Found· C, 38 8; H, 3 1; $C_8H_7O_4$ Br requires C, 38 9; H, 2 8%). It was identical with a sample of 5-bromo-4-methoxy-salicylic acid prepared from a pure sample of 4-methoxy-salicylic acid.

The bromo acid was esterified by boiling with anhydrous methyl alcohol and a little concentrated sulphuric acid for 12 hours On allowing to stand overnight crystals of the ester separated out When recrystallised from methyl alcohol-acetic acid mixture it came out in the form of rhombohedral plates melting at 145–46°, agreeing with the description of the ester by Potter Rice[6] who obtained it by a different method

(2) *Using absolute alcoholic potash* —Kanugin (0·75 g) was treated with absolute alcoholic potash (30 c c of 8% solution) and the mixture refluxed for 6 hours under anhydrous conditions The solid did not go into solution easily and only after 2½ hours solution was complete After 6 hours, the solvent was completely removed, water (30 c c) added and the solution filtered through a plug of cotton-wool When the filtrate was acidified, a crystalline solid separated in good yield The solution along with the solid was extracted with ether twice and the ether solution shaken with aqueous sodium bicarbonate to separate the acidic component (A) The ether layer was finally washed with water and evaporated The residue was a liquid which soon solidified. It was filtered, washed with a little water and crystallised twice from hot water when it came out as colourless thin rectangular plates melting at 65–67°. Mixed melting point with an authentic sample of ω: 4-dimethoxy-2-hydroxy-acetophenone was undepressed. It gave a reddish brown colour with ferric chloride and did not respond to the methylenedioxy group test The 2:4-dinitrophenyl-hydrazone of the ketone prepared in the usual manner was crystallised from ethyl acetate, when it came out as bright red rectangular plates It melted at 218–20° alone or when admixed with the 2. 4-dinitro-phenylhydrazone of synthetic ω: 4-dimethoxy-2-hydroxy acetophenone

On acidifying the bicarbonate extract (A) with hydrochloric acid a crystalline solid was obtained. It was filtered, washed with a little water and purified by crystallising twice from methyl alcohol from which it sepa-

rated as big rectangular prisms with a tendency to taper at the ends and melting at 212–14° This was identical with myristicic acid obtained in the other method of hydrolysis

Demethylation of Kanugin Nor-Kanugin (Robinetin)

A solution of kanugin (0·5 g) in phenol (3 c c) was treated with hydriodic acid (10 c.c of d 1 7) The mixture was heated at 150–60° for 1 hour It was then cooled, diluted with water (50 c c) and free iodine decomposed by means of sodium sulphite The yellow solid that separated out was filtered, washed repeatedly with hot water and purified by crystallising it from aqueous alcohol when it came out as yellow rectangular plates, melting at 320–25° with decomposition (Found in the air-dried sample C, 55 9, H, 4 1; $C_{15}H_{10}O_7$, H_2O requires C, 56 2, H, 3 7%) The compound was sparingly soluble in hot water and moderately in alcohol and acetic acid. Its alcoholic solution exhibited a brilliant green fluorescence It gave a dark olive green colour with ferric chloride and a red precipitate with lead acetate in alcoholic solution In concentrated sulphuric acid it dissolved to form a yellow solution without fluorescence

Nor-Kanugin Acetate

The acetate of nor-kanugin was prepared by boiling it (0·1 g.) with acetic anhydride (3 c c) and a drop of pyridine for an hour and a half. The anhydride was then removed under reduced pressure and the white solid left behind was purified by crystallisation from absolute alcohol It came out in the form of colourless narrow rectangular prisms, melting at 223–25° The mixed melting point with a sample of the acetate of robinetin was not depressed (223–25°).

Nor-Kanugin Methyl Ether

A solution of nor-kanugin (0·1 g) in anhydrous acetone (25 c c.) was treated with dimethyl sulphate (0 3 c c) and anhydrous potassium carbonate (2 g.). After refluxing for 8 hours, the potassium salts were filtered off and the residue washed with a little acetone When the solvent was distilled off, the methyl ether was obtained as a white crystalline solid. It was purified by crystallisation from alcohol when it appeared as narrow rectangular plates melting at 148–49°; the mixed melting point with *robinetin* methyl ether (synthetic) was undepressed (Found in the air-dried sample: C, 61·9; H, 6·0; OCH_3, 38·9 and loss on drying *in vacuo* 5 0 $C_{20}H_{20}O_7$, H_2O requires C, 61 5; H, 5 6; OCH_3 39 7 and H_2O loss 4 6. Found in samples dried at 110° *in vacuo*. C, 64 9, H, 5 5; $C_{20}H_{20}O_7$ requires C, 64 5; H, 5·4%)

Summary

Kanugin $C_{19}H_{18}O_7$ yields myristicic acid and *p*-methoxy salicylic acid when decomposed with aqueous alcoholic potash and myristicic acid ω: 4-dimethoxy-2-hydroxy-acetophenone when decomposed with absolute alcoholic potash. Nor-kanugin has been identified as robinetin by a comparison of the flavonols and their derivatives It is, therefore, concluded that kanugin is 3:7:5'-trimethoxy-3'·4'-methylenedioxy-flavone. The crystalline components of the seeds, flowers and root bark of *Pongamia glabra* are compared

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A NOTE ON SPECTRAL INTENSITY CHANGES IN HIGH-FREQUENCY GLOW DISCHARGE IN AIR

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Asundi and J. Singh[1] have recently drawn some important conclusions about the relative strengths of the first positive and second positive band systems of nitrogen excited by h f discharge in rarefied air They observed a change in the colour of the glow when the frequency of oscillation was changed This happened abruptly at a critical frequency of 735 k c. below which the first positive system is stronger than the second positive system and above which the reverse is true The change in colour is attributed by them to the change in intensities of these two band systems.

The authors have referred to the work of Brasefield[2] who has investigated the variations in the electron velocity in the h f discharge He extrapolated the velocity of the exciting electrons in the h f discharge from the curves (got from independent experiments) representing the variation in the ratio of the intensities of two neighbouring lines with the uniform velocities of the electrons employed for excitation This method will be correct if the discharge gives rise to uniform electron velocities. This is not true as the electrons undergo a velocity distribution in the h.f discharge Thus it is not possible to draw any quantitative conclusion regarding the mean electron velocity from the above method The deviations of Brasefield's results from the actual values of the electron velocities, occurring in the h f. discharge, cannot be estimated unless some new method is tried which takes into consideration the distribution of electron velocities The general conclusions about (1) the increase in electron velocity with the decrease in the frequency of oscillation; (2) the increase in electron velocity with the increase in excitation voltage; (3) the decrease in electron velocity with the increase in pressure, may be true but no qualtitative conclusions are possible

Asundi and J Singh have assumed that the output voltage of the oscillator was constant for all the frequencies This is contrary to our experience of Hartley circuits The output voltage varies considerably with the change in frequency At the same time the conductivity of the discharge being different at different frequencies. the load on the oscillator will vary at

different frequencies and may cause a change in the output voltage It is known that unless the Hartley circuit is meant to deliver a considerably high power the output voltage changes with the load. Data with regard to the modified Hartley circuit used by Asundi and J Singh giving a constant voltage output at different frequencies and loads would have facilitated the correctness of the above assumption It would have been better if the constancy of voltage was checked and its absolute value noted. These conditions being not defined, it is quite likely that the change in the electron velocity which is responsible for the change in the relative intensities of the two band systems may be due partly to the change in voltage and partly to the change in frequency or to the change in voltage only.

Again there is no mention of the pressure at which the investigations were made and this is a very significant factor According to Brasefield's simplified mechanism of the h f discharge, a decrease in frequency will increase the electron velocity, because the time for which electric force will act on the electron will be longer at lower frequency If this is correct, then with a known change in frequency the resulting change in the electron velocity will depend on the mean free path of the electron and thus on the pressure. This change in electron velocity with a known change in frequency will also depend on the voltage of excitation as the velocity will depend on the electric force acting on it. Thus for a particular applied voltage, there will be a pressure above which a change in frequency will not change the electron velocity This will be when the m f p for the electron will be smaller than the distance travelled by it in the time of half a cycle at the highest frequency. Asundi and Pant[3] have also observed that the phenomena get complicated at high pressures. This is due to the small m.f p. of the electrons at high pressures

A phenomenon of the colour change in the glow of the h.f discharge in air was lately observed by us while doing probe study of the h.f discharge The frequency range was higher than that used by Asundi and J. Singh (4 to 15 m.c.). A sudden change in colour was observed when the pressure in the discharge tube was being lowered. The change was abrupt at a certain pressure The value of this critical pressure was found to vary with excitation voltage as well as the frequency. In view of this, it appears that the change in colour is a complicated phenomenon associated with several parameters like pressure, frequency, excitation voltage, etc As an example, the following Tables I and II will give an idea as to how either of these parameters is susceptible to change with variation in the other The observations given here were taken with a cylindrical tube having external sleeve electrodes.

TABLE I

Frequency in megacycles sec	Critical Pressure in mm at	
	1000 V	1300 V
12	0 24	0 54
9	0 34	0 69
7	0·40	0·76
4	0 51	0·89

TABLE II

Voltage	Critical Pressure in mm at Frequency	
	4 mc /sec	9 mc /sec
800	0 20	
1000	0 51	0 34
1250	0 73	0 56
1400	0 85	0 68

The tube was connected through drying system and oil manometer to a Cenco Hyvac pump The discharge was excited by h f oscillations from a Hartley circuit, the frequency of which was changeable from 4 to 15 megacycles. The h f voltages were measured by a thermionic voltmeter specially designed for the purpose. The frequency was measured by a General Radio absorption type of wavemeter. Table I gives the variation of critical pressure with frequency of oscillation at two excitation voltages, while Table II shows its variation with the voltage at two different frequencies

We agree that the relative changes in the two band systems as observed by Asundi and J Singh may have been brought about by a change in electron velocity, but whether the critical velocity can be attributed to a change in frequency alone is a doubtful point in the absence of data about the other variables For some time we have been investigating several other aspects of h f discharge quantitatively, the results of which will be communicated in due course.

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RADIATION BALANCE OF THE LOWER STRATOSPHERE

Part I. Height Distribution of Solar Energy Absorption in the Atmosphere

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Abstract —A study of the radiation balance of the atmosphere involves the determination of the absorption and emission of radiant energy due to the different constituents of the atmosphere In the stratosphere below 50 km., these are mainly ozone, CO_2 and water vapour The major part of the absorbed energy is from solar radiation, the actual absorption at different levels being determined by the absorption coefficients of these gases and their vertical distributions In this paper, a detailed survey is made of all the available data and of the recent methods developed for using such data, and after proper selection, curves are prepared giving the solar energy absorbed by different quantities of O_3, CO_2 and H_2O. These are used to calculate the absorption of solar energy per unit volume and per unit mass in different 2 km. layers for certain vertical distributions of the constituents. It is seen that the mass density of absorption due to ozone above 50 km. becomes much larger than that due to CO_2 and H_2O while in the region below 30 km., they become comparable Water vapour becomes more and more effective as we approach the earth

§ 1. Introduction

The investigation of the important problem of radiation balance of the earth's stratosphere involves the study of the absorption and radiation of energy due to the different absorbing constituents of the atmosphere. Gowan[1] has worked out in two papers the effect of ozone on the temperature of the upper atmosphere. At the time when he wrote his papers, little was known about the detailed height distribution of atmospheric ozone Later work by Götz, Meetham and Dobson,[2] Regener,[3] and the American workers[4] has provided important knowledge about this Penndorf[5] has used some of these results to calculate the heating and cooling of the ozonosphere. But he considered only the ultra-violet absorption due to ozone, without taking into account the visible absorption in the Chappuis band which also plays a part, and neglected the effect of carbon dioxide and water vapour. In a

later paper, Godfrey and Price[6] have investigated 'the thermal radiation and absorption in the upper atmosphere' but have concerned themselves mainly with the ionosphere above 100 km, where the main absorbing constituent is oxygen. On the other hand, Elsasser[7a] in his recent investigation of 'the heat transfer by infra-red radiation in the atmosphere' mainly deals with the region below about 10 km., where water vapour is the predominant absorbing substance. As far as the lower stratosphere is concerned, it is clear that the absorption and emission of radiation is governed almost entirely by ozone, carbon dioxide and water vapour.[8] Oxides of nitrogen and some polyatomic gases like methane, ethylene, etc, which have some absorption bands, usually occur in variable and very small quantities and are probably unimportant Recent investigations of atmospheric absorption in the infra-red by Adel and Lampland,[9] the study of the water vapour spectrum by Weber and Randall[10] and of CO_2 absorption in the infra-red by Martin and Barker,[11] and the development of methods of using such data introduced by Schnaidt,[12] Elsasser,[7] Callendar,[13] and Strong[14,15] supply important material for a reconsideration of the subject

The total inflow of radiant energy from different sources into any layer of the atmosphere consists of (i) the incident solar radiation, (ii) the terrestrial radiation from the surface of the earth, and (iii) the radiation from the different atmospheric layers above and below the layer under consideration, which depends upon their composition and temperature The loss of radiation by the layer consists of the radiation from both sides of the layer, assuming it to radiate at its temperature in those regions where it has selective absorption and in proportion to its effective absorption coefficient The difference between the absorption and emission by the layer will give the net radiation used up in heating the layer, and if there is radiation balance, this quantity will be zero. This is equivalent to the condition that at any level in the atmosphere where there is radiation balance, the incident solar energy flux is equal to the net upward flux due to radiation from all the gaseous layers and the earth

The investigation therefore can be divided into the following sections:—

(i) An examination of the nature and amounts of the different absorbing gases at different levels in the atmosphere. We shall confine our attention to the region below 50 km.

(ii) Collection and selection of the necessary data regarding the absorption coefficients of the constituent gases throughout the spectrum.

(iii) Calculation of the vertical distribution of solar energy absorption in the atmosphere.

(iv) Preparation of radiation charts for the three main gases (ozone, carbon dioxide and water vapour) of the atmosphere below 50 km., suitable for calculating the net radiation from a given column of absorbents

(v) Calculation of the equilibrium temperatures for known vertical distributions of ozone like those at Tromsø, Arosa, Poona, etc , and assumed distributions of CO_2 and water vapour

It is the purpose of this paper to consider the absorption side of the problem, covering the first three items The radiation side and the linking up of the two sides will be taken up later in two papers.

§ 2 The Solar Energy Curve

The solar energy received at the earth is a parallel beam radiation The intensity of the incident solar radiation outside the earth's atmosphere is calculated by using Planck's relation on the assumption that the sun radiates as a black body at 6000° K. This gives the total energy radiated out from unit area of the sun's disc as

$$R = \sigma T^4 = 1767\ 6 \text{ cal. cm}^{-2} \text{ sec}^{-1}$$

The energy received at the outer limit of the earth's atmosphere will be the solar constant, S, and is given by

$$S = R \cdot r^2/D^2 = 2\ 306 \text{ cal cm}^{-2} \text{ min}^{-1},$$

where r is the sun's radius and D the earth's mean distance from the sun. This is considerably higher than the observed value, *viz* , 1 925 cal cm.$^{-2}$ min.$^{-1}$, the mean value given by Abbot [16] Abbot's value is however obtained neglecting the absorption of solar energy by ozone in the ultra-violet (Hartley) band which is about 6 26% Including this, S becomes 2·045 cal. cm.$^{-2}$ min^{-1} Still there is discrepancy between this value and the above calculated value This is due either to the sun's assumed effective temperature (6000° K) being too high, or the fact that the sun might not be radiating strictly as a black body.[17] In all further calculations, the sun is taken as a black body at 6000° K. and the solar constant as 2 045 cal. cm^{-2} min.$^{-1}$, which is Abbot's value corrected as mentioned above; thus the solar energy received by one sq cm at the outer limit of the earth's atmosphere is given by simply multiplying the corresponding energy radiated from one sq cm of the sun's disc by the factor: $S/R = 1\ 929 \times 10^{-5}$. This is equivalent to taking the effective temperature to be nearly 5823 ° K. for the total radiation and, rather inconsistently, to be 6000° K for the distribution of radiant energy in the solar spectrum Any error that might be caused in doing so will be of a numerical nature, and can easily be corrected by making a corresponding slight change in the above multiplying

factor. Tables I, II, III give the solar energy contained in the different absorption bands of ozone, CO_2 and water vapour, as it is received at the outer limit of the earth's atmosphere.

§ 3 Ozone Bands

(1) *Ultra-violet (Hartley) Band*. 2000-3300 Å —(*a*) Data by Meyer,[18] Lauchli,[19] Fabry-Buisson,[20] Ny Tsi-Ze and Choong[21] are available Those by the last named authors (Fig 1) were used as being the most detailed

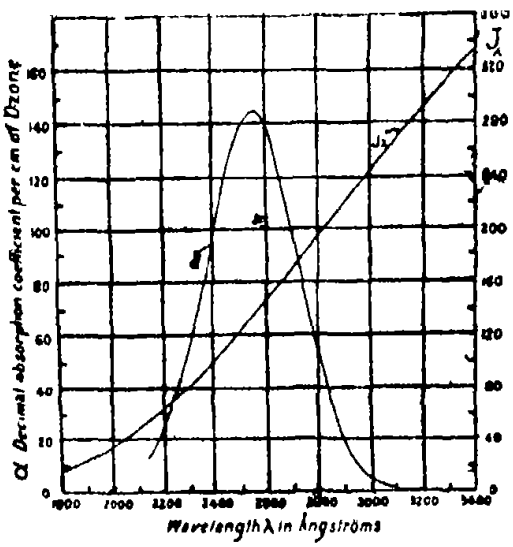


Fig 1 α, the decimal absorption coefficient per cm of ozone at N T P in the Hartley band according to data by Ny Tsi-Ze and Choong Shun-Piaw J_λ is the intensity of the incident solar radiation just outside the earth's atmosphere
Unit of $J_\lambda d\lambda$ = cal cm^{-2} sec^{-1}

The curve gives the decimal absorption coefficient α per cm of ozone at N T P at different wavelengths, Beer's law ($I = I_0 \times 10^{-\alpha x}$) being assumed to hold for each wavelength Curves were prepared, using Beer's law, giving absorption from wavelength to wavelength due to known quantities of ozone The transmission curves showing how the incident solar energy curve gets modified due to passage through different quantities of ozone are given in Fig 2 Graphical integration of similar absorption curves gave the solar energy aborption for each quantity of ozone, from which a general curve (Fig 3) was obtained, and this was used for further calculations.

(*b*) *Alternative method.*—Chapman[22] in his paper on "The atmospheric height distribution of band-absorbed solar radiation" suggested that the form

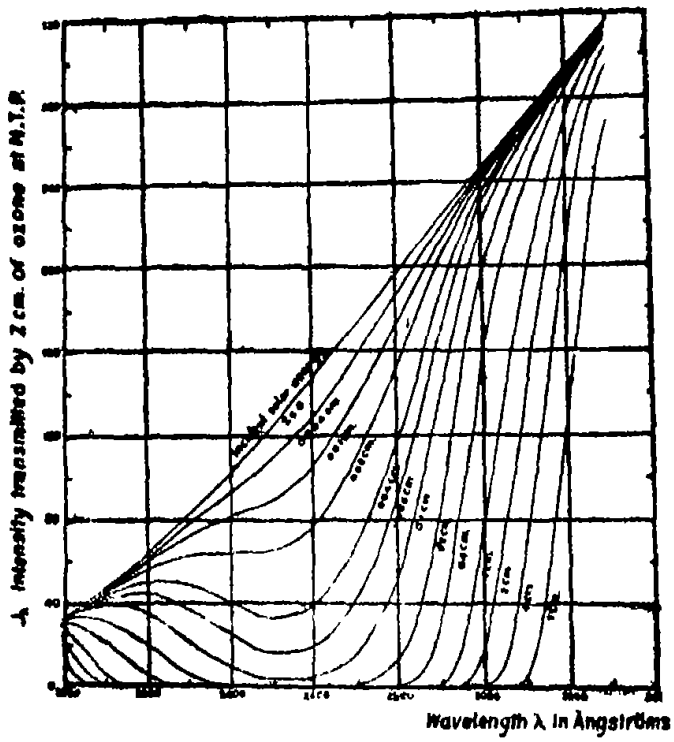


FIG 2 Intensity of solar radiation in the Hartley band after passage through different thicknesses of ozone in the earth's atmosphere

Unit of $J_\lambda d_\lambda$ = cal cm^{-2} sec^{-1}

of the absorption curve can be expressed by the normal error equation:

$$a = a_0 e^{-h^2(\lambda-\lambda_0)^2}, \qquad (1)$$

where a_0 = peak value of a, λ_0 = wavelength corresponding to a_0, and h determines the spread of the band which can be obtained by plotting* log a against $(\lambda - \lambda_0)^2$. Then the fractional absorption at any wavelength λ by Z cm. of ozone will be $1 - e^{-Z\beta e^{-h^2(\lambda-\lambda_0)^2}}$, where $\beta = 2{\cdot}303\, a_0$. If the solar energy curve in the region between $\lambda_1 = 2000$ Å and $\lambda_2 = 3300$ Å, $(\lambda_1 < \lambda_0 < \lambda_2)$, is assumed to be of the linear form $J_\lambda = k + m\lambda$, the total solar energy absorption by Z cm. of ozone in the band within the limits λ_1 and λ_2 becomes.

* Läuchli and Fabry-Busson plot log a against λ and give the following empirical formulæ for the region 2800-3350 Å:

log a = 17·58 − 0·0564·λ .. .. (F. & B.)

log a = 16·74 − 0·0536·λ .. . (L.)

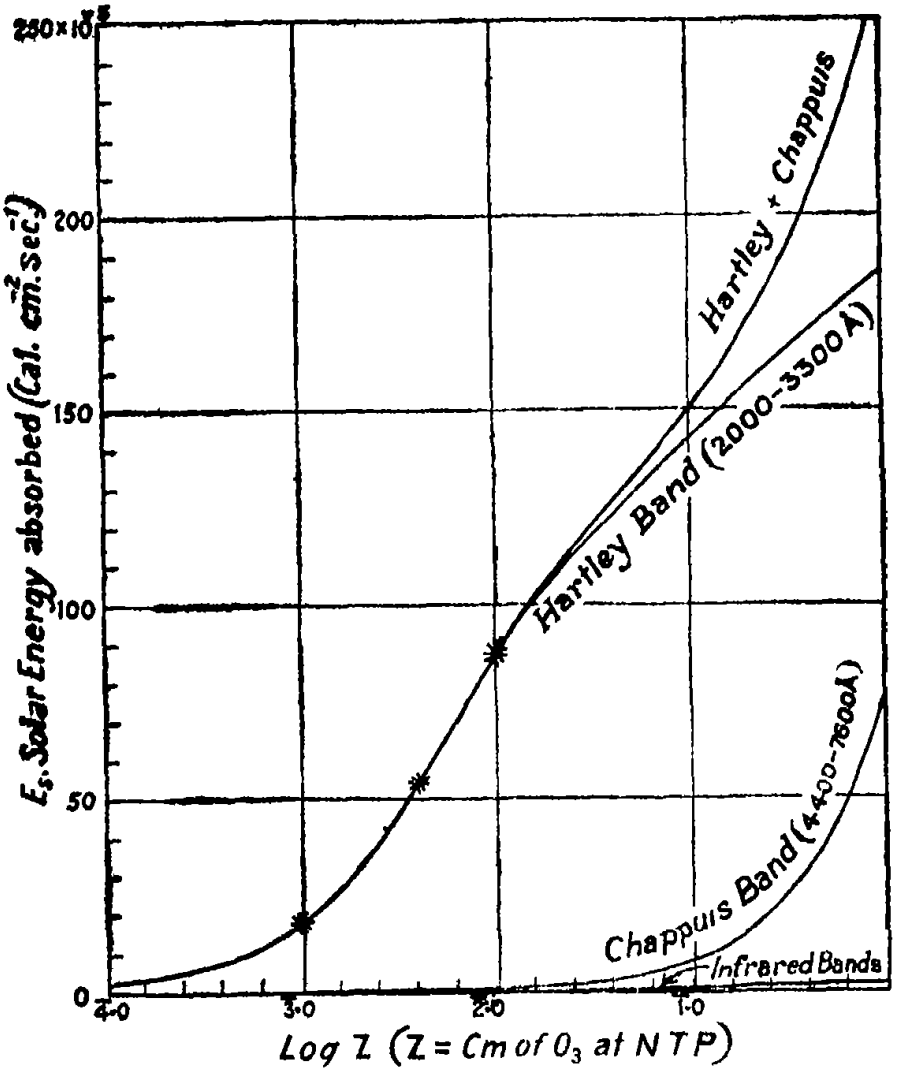


FIG 3. Absorption of solar energy by Z cm of ozone at N T P in the different bands

$$E_s = \int_{\lambda_1}^{\lambda_2} J_\lambda \left(1 - e^{-Z\,\beta e^{k''(\lambda-\lambda_0)^2}}\right) d\lambda$$

$$= \int_{\lambda_1}^{\lambda_2} (k + m\lambda)\left(1 - e^{-Z\cdot\beta e^{-k''(\lambda-\lambda_0)^2}}\right) d\lambda$$

The integral can be evaluated† and shown to be.

† I thank Prof D D. Kosambi for his help in the solution This method for a limited nd can be extended to similar single or composite absorption bands of any gas.—Author.

$$= J_{\lambda_0} \frac{\sqrt{\pi}}{2\sqrt{p}} \qquad m \qquad (2)$$

where $S_1 = \sum_1^{\infty} (-1)^{n+1} \frac{p}{n!\sqrt{n}} [\phi(\sqrt{n}A) + \phi(\sqrt{n}B)]$,

$S_2 = \sum_1^{\infty} (-1)^{n+1} \frac{p^n}{n!\,n} [e^{-nA} - e^{-nB}]$,

and $p = \beta Z$, $A = h^2(\lambda_1 - \lambda_0)^2$, $B = h^2(\lambda_2 - \lambda_0)^2$, $J_{\lambda_0} = k + m\lambda_0$,

and ϕ denotes the error function given by $\phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$.

The infinite series S_1 and S_2 in equation (2) can be evaluated by using tabulated values of $\phi(x)$ and e^{-x}. It is found/that S_1 is the main term, while S_2 is a correction term being the difference of two small and nearly equal quantities. E_z was evaluated for different values of Z of ozone Three such values (for Z = 001 cm , 004 cm , ·01 cm.) are shown by stars on the curve relating to the Hartley band in Fig 3, showing good agreement with the values obtained by the graphical method

In Chapman's paper referred to above, he gets the absorption of energy of radiation between wavelengths λ and $\lambda + d\lambda$ between levels m and $m + dm$, which is $\frac{dS_\lambda}{dm} d\lambda$, $S_\lambda d\lambda$ being the intensity of the incident beam at the level m, and then integrates it over the whole band. In this paper, we do not calculate the density of energy absorption directly, but only the energies absorbed by different finite masses Z cm of ozone when the incident energy J_λ is of the linear form assumed The multiplication of the terms J_λ and α_λ (due to differentiation with respect to m) does not therefore appear in our integrals The actual energy absorption in an atmospheric layer of finite extent will be found by getting the values of the energies absorbed down to the top and base of the layer, beginning at the outer limit of the atmosphere, and then taking their difference This quantity divided by the mass in the layer gives the mass density of energy absorption This is an elementary but practical way of getting the density of energy absorption in the different layers of an atmosphere of any arbitrary composition, the values obtained being averages over these regions. This will give equally good results if the layers are taken sufficiently small

(*c*) It is assumed in accordance with the observations of Vassy[13] that there is no variation of absorption with pressure in the Hartley band. This has been recently verified by Strong.[14]

(*d*) Data by Vassy[24] show that the temperature effect is small and it has been neglected

(2) *Visible (Chappuis) Band:* 4400–7600 Å —This band has been studied by Colange,[26] E Vassy,[25] A Tournaire-Vassy[27] in the laboratory, and by Cabannes and Dufay[28] and Fowle[29d] in the atmosphere Absorption coefficients at 18° C (Fig. 4) from A. Tournaire-Vassy's measurements quoted

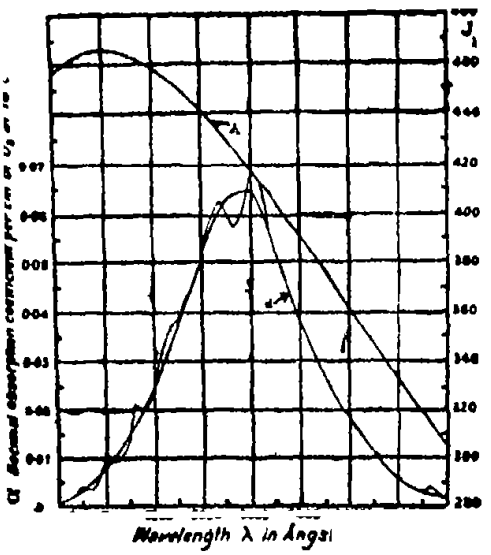


FIG 4 α, the decimal absorption coefficient per cm of ozone at N T P in the Chappuis band, and J_λ, the intensity of the incident solar radiation just outside the earth's atmosphere. The coefficients are for a temperature of 18° C, and unit of $J_\lambda d\lambda$ = cal cm $^{-2}$ sec $^{-1}$

in detail by Götz[29] were used Since this band lies in a region near the peak of the solar energy curve and is much wider than the Hartley band, it plays a not unimportant part in the absorption of solar energy Curves similar to those for the Hartley band showing the solar energy absorption by different path lengths of ozone were prepared (Fig. 3).

It will be seen that the Chappuis band becomes important for ozone values higher than about 0·1 cm , *i.e.*, below about 25 km For places in high latitudes where the sun will be low for many hours, this band will play an important role This is clearly shown in Fig. 5, which gives the actual solar energy absorption at different levels in the atmosphere for an ozone distribution like that at Tromsø (Lat. 69°40′ N.), for different zenith distances. It is interesting to note that the solar energy absorption curve for the Chappuis band closely follows the ozone distribution curve, since the energy

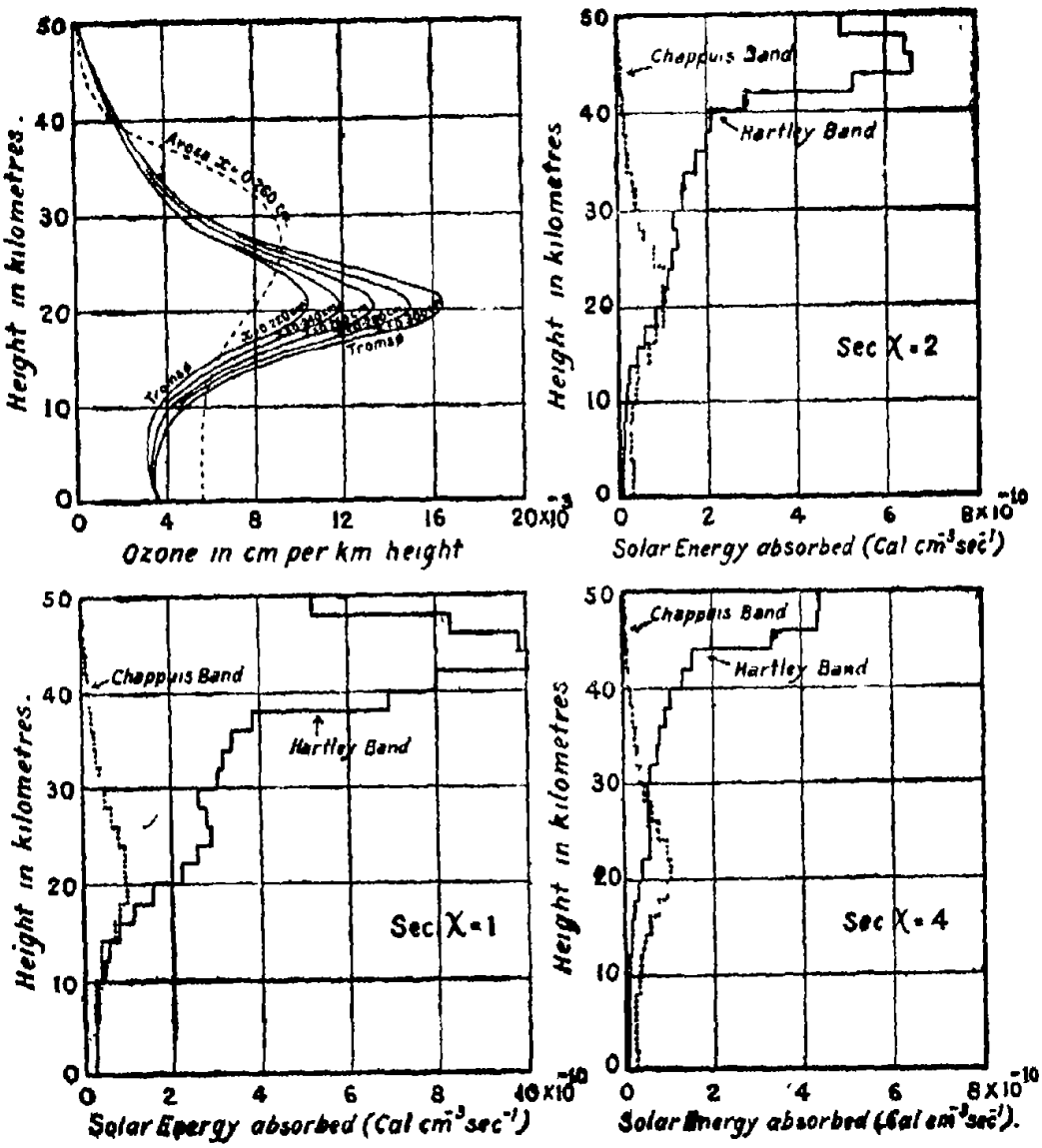


FIG 5 Vertical distribution of ozone at Tromsø and the corresponding rates of absorption solar energy in the Hartley and Chappuis bands for different zenith distances x of the sun

absorption varies practically linearly with ozone quantity even up to 1 cm of ozone.

There are no measurements of the pressure effect on this band. The study of the temperature effect by E. Vassy[35] shows an increase of absorption

coefficient with decrease of temperature, being about 12% greater when the temperature is reduced from 20° C to − 40° C But the values given are only relative, Colange's value for the maximum absorption coefficient at room temperature being assumed as 0 05. Cabannes and Dufay have also used Colange's values to determine the ozone content of the atmosphere But the amounts of ozone they have thus obtained seem to be too high, suggesting that the absorption coefficients are too low Actually in the ozonosphere, lower temperatures than room temperature and hence higher values of the absorption coefficients have to be accepted The values which are quoted by Götz and used in our calculations are about 36% higher than Colange's values This is a change on the correct side, though it may not be quantitatively correct A detailed experimental study with simultaneous observations both in the visible and the ultra-violet regions is still necessary to clarify the matter.

(3) *Infra-red Bands at* 4 75 μ, 9·6 μ and 14 1 μ —These are comparatively unimportant for the calculation of the absorption of solar energy, since the solar energy curve goes down rapidly in the infra-red This will be clear from Fig. 3 and Table I which give the solar energy contained in the different ozone bands and the relative absorptions produced by them. Still, the calculations were completed as they are useful for the consideration of the radiation side of the problem.

TABLE I

Intensity of solar radiation $[E_\lambda]_{\lambda_1}^{\lambda_2}$ *in the different ozone bands just outside the earth's atmosphere and the relative absorptions of energy*

Unit of intensity = 10^{-6} cal cm^{-2} sec^{-1}

Band	Range	$[E_\lambda]_{\lambda_1}^{\lambda_2}$	Energy absorbed by Z cm. of ozone at N T.P. when kept at a pressure of 25 mb.			
			Z = 001 cm.	Z = 01 cm.	Z = 1 cm.	Z = 1 cm.
Hartley Band	2000–3300 Å	213 5	18 1	80·3	142 5	186 5
Chappuis Band	4400–7000 Å	1700 5	0·08	0 81	8 08	77·4
Infra-red 4·75 μ Band	4·65–4 90 μ	2 66	0 04	0 13	0 40	1 19
9·6 μ ,,	9·3–10 1 μ	0 58	0 014	0·05	0·14	0 39
14·1 μ ,,	12 0–16·5 μ	0 78	0 006	0 02	0 06	0·17
Total for all bands		1517 9	18·3	87 3	151 2	265·7

(*a*) For the 9·6 μ band, Adel's [9] curves on the atmospheric absorption measured at Lowell Observatory were used to calculate the absorption

coefficients (Fig. 6) by a method‡ of reduction and elimination, the effective pressure being taken to be 25 mb., which is roughly the pressure at the centre of gravity of atmospheric ozone. The recent values obtained by

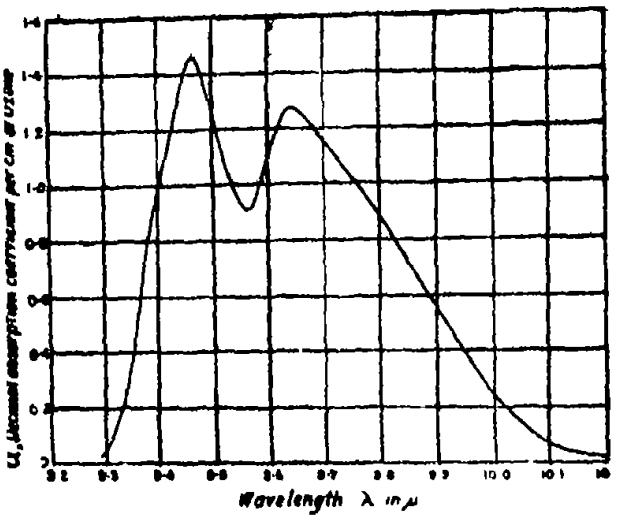


Fig. 6 α, the decimal absorption coefficient per cm of ozone at N.T.P. in the 9·6 μ infra-red band calculated from the atmospheric measurements of Adel and Lampland.

Strong[14] with the apophyllite residual ray apparatus gave $\alpha = 0{\cdot}8$ to $1{\cdot}0$ per cm. of O_3 at N.T.P. for a gas pressure of 25 mb. and these agree well with those deduced from Adel's data. All old curves gave extremely low values, for example K. Ångström's[30] and Ladenburg and Lehmann's[31] curves gave values of α to be .005 to .09 per cm. of ozone, Gerhard's[32] curves gave $\alpha = .004$ to .019, and curves by Hettner and his co-workers[33] gave $\alpha = .035$.

(*b*) For the bands at 4·75 μ and 14·1 μ, curves recently obtained by Hettner and his co-workers[33] are available. But the quantity of ozone

‡ Out of the different series of observations which Adel gives for the atmospheric transmission in the region 8–11 μ, series A, B and E refer to the same air mass 1·6 but to different water vapour contents, *viz.* 41·5, 21·4 and 3·2 mm of ppt H_2O. Detailed knowledge of the absorption due to CO_2 in the same region (8–11 μ) is available from Barker and Adel's paper (*Phy. Rev.*, Vol. 44, 185, 1933). The total ozone content of the atmosphere was assumed to be the same for the three series, accepting Dobson's mean annual value for the latitude 35° N. of Lowell Observatory as 0·240 cm. at N.T.P. The total CO_2 content was also taken to be the same for the three series, accepting the value 240 cm. at N.T.P. This enabled the effects due to water vapour, CO_2 and ozone to be separated, so that by eliminating the effects of water vapour and CO_2, the absorption due to ozone alone could be calculated at each wavelength. Fig. 6 gives the mean decimal absorption coefficient α obtained from the three series, the effective gas pressure being taken to be 25 mb. which is the pressure at the centre of gravity of atmospheric ozone.

mentioned by these authors (30 cm. of 'practically pure' ozone under a pressure of 160 mm of mercury) seems to be too high If the values of the absorption coefficients obtained from Adel's and Strong's observations at 9·6 μ are taken to be correct and Strong's empirical fourth root law for pressure effect is adopted, this quantity would completely black out most of the 9·6 μ band Hettner's curves however show as much as 5% transmission at the peak of the band. Elsasser[76] also in his paper expresses a doubt about this, but disposes of the matter by saying that the true amount may be different owing to the fact that the line-broadening effect of ozone upon itself may be different from that of air upon ozone But this is only a speculation According to Hertz,[34] Eva Bahr[35] and others the line-broadening effect due to the addition of air or of the pure gas obeys the square root law in the case of CO_2 and water vapour The only available laboratory data in the case of ozone are those by Strong who proposes the fourth root law But whichever law is nearer the truth, it is difficult to accept the quantity mentioned by Hettner and his co-workers The best way seems to be to accept Adel's results as correct for the 9·6 μ band and recalculate the partial pressures of ozone in the experiments of Hettner, and thence the absorption coefficients in the other regions The average absorption coefficients k given in the appendix are obtained in this manner, using Elsasser's relation $A = \phi(\sqrt{kZ})$, and the fourth root law proposed by Strong to take into account the pressure effect

(*c*) Though Strong has proposed the fourth root law for the pressure effect, most other workers propose the square root law for the infra-red region in general It is difficult to see why the 9·6 μ band of ozone should be an exception to the square root law The use of the apophyllite residual ray apparatus in Strong's observations necessarily involves the reflection contour characteristic of the material used, and what is obtained is the combined integrated effect of the reflection contour and ozone absorption Results obtained with such apparatus are therefore not strictly comparable with those with sufficient spectral details The use of any higher root law only means less variation of absorption with pressure For the use of any nth root law in this connection, coefficients appropriate to a standard pressure p_0 are to be calculated from observations made at any pressure p on a quantity Z cm. of ozone, using the relation $Z\sqrt[n]{p/p_0}$ For calculations in the ozone bands, the standard pressure p_0 is taken to be 25 mb , which is roughly the pressure at the centre of gravity of ozone. It was also arbitrarily decided to accept the fourth root law for all infra-red bands of ozone, since no other results than those of Strong are available for the pressure effect. For carbon

dioxide and water vapour bands, however, the square root law was used in accordance with the conclusions of Hertz and Eva Bahr. It was seen (Fig. 3) that the actual value of the solar energy absorbed by ozone in all the infra-red bands taken together becomes very small as compared with the absorption of energy in the ultra-violet and the visible regions, and hence it matters very little whether the square root law or the fourth root law is used to take account of the pressure effect.

(*d*) The temperature effect was neglected due to lack of available data In any case, the total absorption being small, the neglect is not important

§ 4 Carbon Dioxide Bands

All CO_2 bands lie in the infra-red region beyond 2μ Still the total CO_2 content of the atmosphere being as large as 240 cm at N T P, it plays a part in the absorption of solar energy, especially in the lower stratosphere.

The important bands are at $2{\cdot}7\mu$, $4\ 3\mu$, $9\text{–}11\mu$ and $12\ 5\text{–}17{\cdot}5\mu$. For the $2{\cdot}7\mu$ band, Barker's[26] curve was used Absorption curves for different quantities of CO_2 were prepared similar to those for ozone, using Beer's law for each wavelength, graphical integration of such curves gave the solar energy absorption for the band For the $4\ 3\mu$ band, Martin and Barker's [11] new curves were used For the remaining two bands, data collected

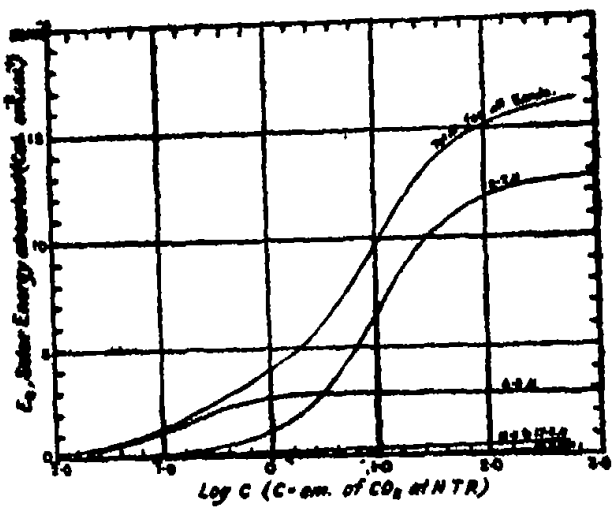


Fig 7 Absorption of solar energy by C cm. of CO_2 at N T P in the different bands

by Callendar[13] were used, adopting his empirical formula $A = 1 - (1 + nc^r)^{-1}$ The comparative importance of the different CO_2 bands for the absorption of solar energy will be seen from Fig 7 and Table II.

TABLE II

Intensity of solar radiation $[E_s]_{\lambda_1}^{\lambda_2}$ *in the different* CO_2 *bands just outside the earth's atmosphere and the relative absorptions of energy*

Unit of intensity = 10^{-5} cal cm^{-2} sec^{-1}

Band	$[E_s]_{\lambda_1}^{\lambda_2}$	Energy absorbed by C cm of CO_2 at N T P					
		C = 01cm.	C = ·1 cm.	C = 1 cm	C = 20 cm.	C = 100 cm.	C = 240 cm
2·66–2·82 μ	12 76	01	0 11	1 07	9·06	11 76	12 38
4 19–4·37 μ	2 87	15	1·15	2 76	2 87	2 87	2 87
9–11 μ	1·33	0	0	0	0 01	0 02	0 05
12·5–17·5 μ	0 72	01	0·04	0 15	0 36	0 46	0 51
Total for all bands	17 68	0 17	1·30	3 98	12 24	15 11	15 81

The square root law was used for the pressure effect and the temperature variation of absorption coefficients was neglected.

It is to be noted that the last two bands partly overlap the corresponding ozone bands, while the first two and also the last overlap the corresponding water vapour bands Absorptions due to the different absorbents in a common band will be additive as long as each is only a few per cent For large absorptions, however, the transmissions will be multiplicative This has to be taken into consideration when actually evaluating the energy absorptions due to a given distribution of the absorbents

§ 5 WATER VAPOUR BANDS

Absorption due to water vapour begins in the near infra-red at about 0 9 μ and extends with varying intensity throughout the infra-red region with a transparent window between 8 and 11 μ Though the maximum amount of water vapour present above the tropopause may not exceed 0 03 cm of precipitable water, the region of absorption is so extensive and some of the bands in the region 2 to 8 μ so intense that even this small quantity contributes an important share to the solar energy absorption The main bands up to 8 μ are shown in Table III.

Complete spectroscopic observations with very small amounts of water vapour such as may be present in the upper atmosphere are not available The lowest quantity for which Fowle[27] gives data is 0 008 cm of precipitable water, while Hettner's[28] data in this region were obtained for about 0 06 cm. of precipitable water. There is general agreement between the values

TABLE III

Intensity of solar radiation $[E_\lambda]_{\lambda_1}^{\lambda_2}$ *in the different water vapour bands just outside the earth's atmosphere and the relative absorptions of energy in the region 0·9 μ to 8 μ*

Unit of intensity = 10^{-3} cal cm.$^{-2}$ sec.$^{-1}$

Author	Band	Range in μ	$[E_\lambda]_{\lambda_1}^{\lambda_2}$	Energy absorbed by W cm of ppt H_2O			
				W = ·0001 cm	W = ·001 cm	W = ·008 cm	W = ·04 cm.
Hettner	ρ	0·89–0·99	200·8	0·01	0·13	1·01	5·00
	φ	1·08–1·19	139·4	0·02	0·17	1·36	6·68
	ψ	1·27–1·53	185·1	0·15	1·41	10·55	42·78
	Ω	1·70–2·02	95·0	0·09	1·07	7·99	29·66
Fowle	κ_1	2·2–3·2	91·5	2·45	7·74	21·60	45·58
	κ_2	3·2–4·0	24·9	0·61	1·93	5·40	11·50
	Y	4·0–4·9	12·8	0·48	1·50	4·15	8·32
	/*	4·9–8·0	12·6	0·62	1·95	5·08	8·68
Total for all bands			702·1	4·43	15·90	57·14	158·20

* Calculations were made separately for the component bands Z_1 (4·9–5·4 μ), Z_2 (5·4–5·9 μ), Z_3 (5·9–6·4 μ), Z_4 (6·4–7·0 μ) and Z_5 (7·0–8·0 μ) as mentioned by Fowle and added up

obtained from the two measurements only in the region up to 2 μ and for small values of precipitable water For the range 2 to 8 μ, where the absorption is so large as to blackout the band heads in Hettner's observations, the results obtained by the two authors are not comparable and Fowle's data have been used

In a recent paper, Fox and Martin[39] have investigated the absorption spectrum of water in the three states and in solution in carbon tetrachloride in the region 2·5–7·5 μ They have however explored the spectrum of *water vapour* only in the region 2·5 to 2·85 μ From the molecular extinction coefficients they have presented, it seems that the limits of the band are narrower than those given by Fowle, or the wings of the bands are too weak for detailed measurements Calculations for the same quantity of precipitable water (W = ·008 cm) which Fowle had used show that the average absorption over the region 2·5 to 2·85 μ is 45·6%, whereas over the region 2·2 to 3·2 μ it becomes 15·3% The latter value may be compared with Fowle's figure 23·6% for the same region. Fowle's figure has been used in our calculations

Another interesting point mentioned by Fox and Martin is that the 4·7 μ band found in the solid and liquid states of water has no counterpart

in the vapour spectrum and has therefore been attributed by them to associated water molecules. On the other hand, Fowle's curves for W = 008 cm. of precipitable water show as much as 30% absorption in this region, and this cannot be attributed to CO_2, as there is no CO_2 band at 4 7 μ In any case, from the point of view of our present calculations of the solar energy absorption, this does not affect our general conclusions seriously

For the region 0 9 μ to 2 μ, Hettner's curves giving more spectral details were reduced in a way similar to that used for the Hartley band of ozone, and the energy absorption was obtained by graphical integration Beyond 2 μ, Fowle's results were used, Elsasser's error function being applied over the subregions to get the energy absorptions due to different quantities of water vapour Table III and Fig 8 summarise the results. It is to be noted that in the first region up to 2 μ, the absorption is weak though the solar energy

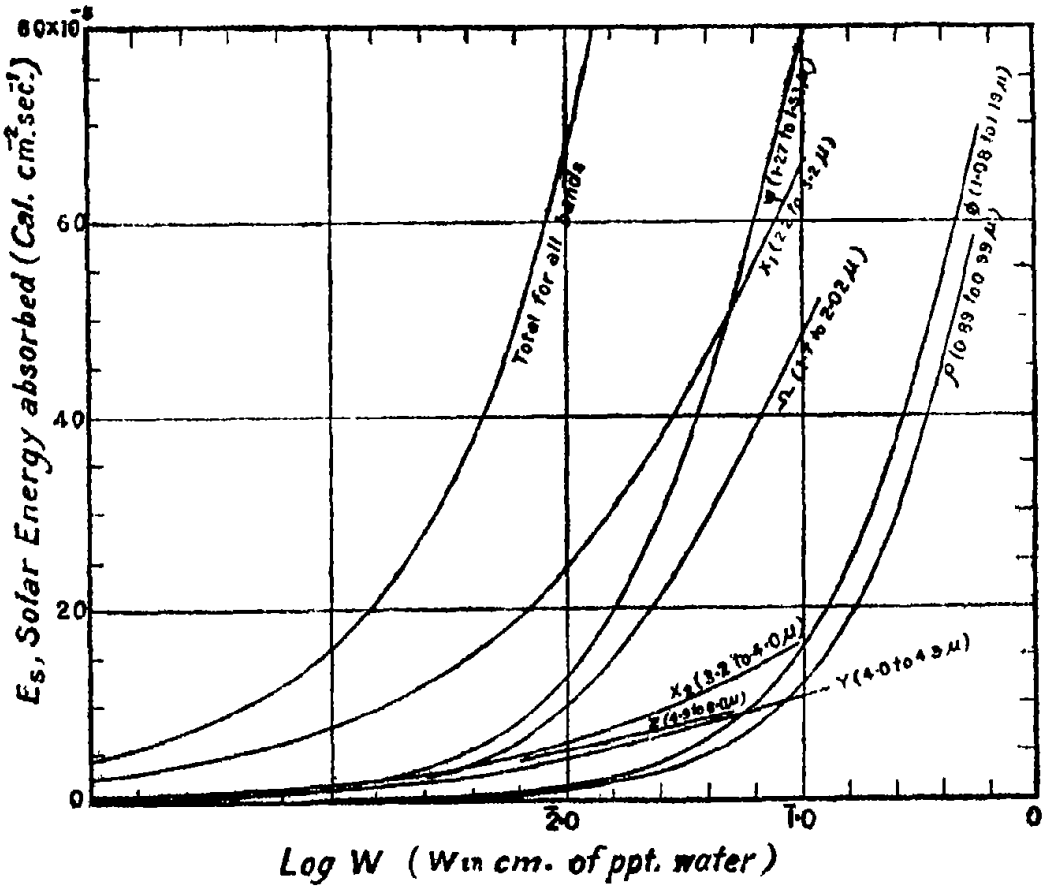


Fig. 8. Absorption of solar energy by W cm. of precipitable water in the different bands.

is large, whereas in the second region the energy is small but the strong absorption takes away most of the energy. The bands in the second region are therefore effective in the uppermost layers of the atmosphere

The temperature effect is negligible for the values of water vapour involved in the upper atmosphere, as indicated by Elsasser[7c] and Cowling [8] For the pressure effect, the square root law was used as for carbon dioxide

§ 6. Height-Distribution of the Constituents and the Calculation of Solar Energy Absorption

(*a*) *Ozone* —The vertical distribution of atmospheric ozone has been investigated for the following places: —

(i) At Arosa[2a] in Switzerland

(ii) At Tromsø [2b]

(iii) At Stuttgart in Germany by Regener [3]

(iv) In U S A by the Bureau of Standards[4] and Explorer II

For the study of the solar energy absorption, the first two cases were selected, the remaining cases can be treated in a similar way The difficulty common to all of them lies in the fact that the distribution of ozone in the uppermost layers (above 40 km) is not known with sufficient accuracy, while ozone quantities at these levels are important for solar energy absorption.

For the present calculations, the ozone content above 50 km. was neglected The atmosphere up to 50 km was divided into 2 km layers, and the ozone content in each layer and also down to the base of each layer obtained graphically The temperature effect on absorption was neglected. The energy absorption down to the base of each layer was found by using curves similar to the curves of Fig. 3 on a linear scale The energy absorption in each layer was obtained by differences and this divided by the volume of the air in the layer gives the volume density of energy absorption, E_v. The mass density of energy absorption, E_m, is given by dividing the absorption in the layer by the mass of air traversed For a zenith distance χ of the sun, the rate of absorption of energy in any atmospheric layer is proportional to cos χ

Fig. 9 gives the values of E_v and E_m for the ozone distribution at Tromsø (total $O_3 = 0$ 260 cm) Calculations were made for sec $\chi = 1, 1{\cdot}5, 2, 3, 4$ for averaging the results afterwards for the whole of the day, but curves for sec $\chi = 1, 2$ and 4 only are shown here Similar curves have also been prepared for the distribution at Arosa.

(*b*) *Carbon dioxide.*—The total CO_2 content was taken to be 240 cm at N.T P and the vertical distribution was obtained by assuming it to be present throughout the lower 50 km. in the same proportion of the total air

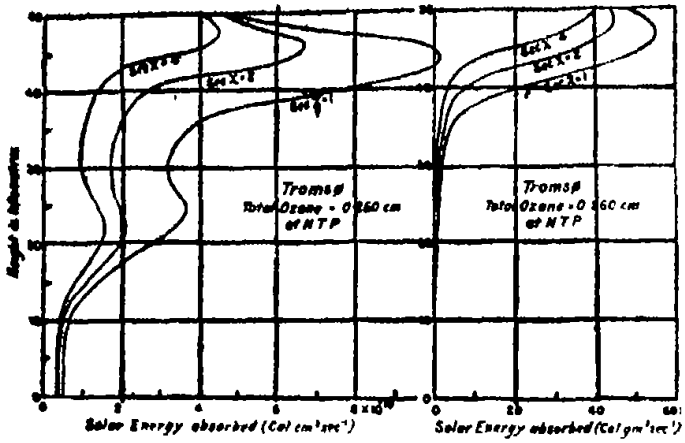


FIG 9 Height distribution of the absorpt on of solar energy by ozone at Total ozone, $x = 0.260$ cm at N T P

as at the surface To get the equivalent quantities for absorption, the amount in each layer was multiplied by $\sqrt{\frac{\bar{p}}{p_0}}$, adopting the pressure distribution in the atmosphere recently given by Penndorf[40] Temperature effect was neglected Curves similar to the curves of Fig 7 on a linear scale were used to find the energy absorption due to different values of CO_2 Fig 10

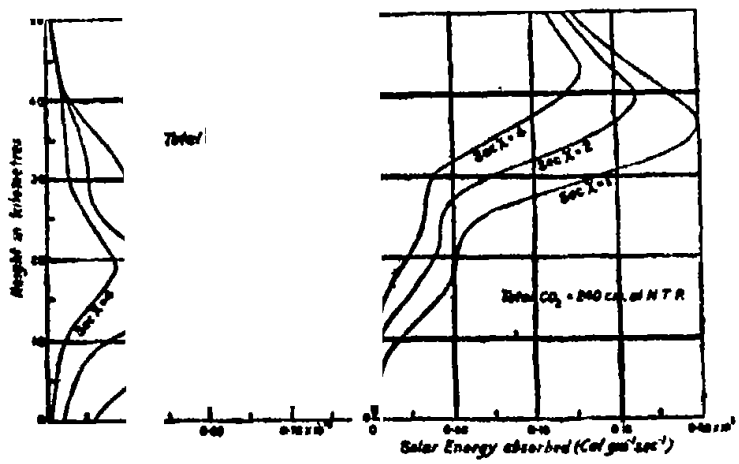


FIG. 10 Height distribution of the absorption of solar energy by carbon dioxide. Total CO_2 content of the atmosphere = 240 cm at N T P and CO_2 assumed to exist in the same proportion at all heights.

gives the absorption of solar energy by CO_2 for three different zenith distances of the sun.

(*c*) *Water vapour.*—No ' measurements ' of the amount and distribution of water vapour in the stratosphere are available. Simpson[41] considered

that the stratosphere contained about 0·3 mm. of precipitable water. This was based on the assumption that the air was saturated at the base of the stratosphere at a temperature of about 220° A Ramanathan[43] pointed out that in the tropics at any rate, the amount of water vapour in the stratosphere should be much less because of the much lower temperatures at the tropopause Brunt and Kapur[43] have given tables with the values of water content ranging from 0 01 mm at the equator to 0 1 mm in the latitude 50° in winter and to 0·17 mm. in summer In a later paper, Brunt[44] regards these as overestimates of the actual values

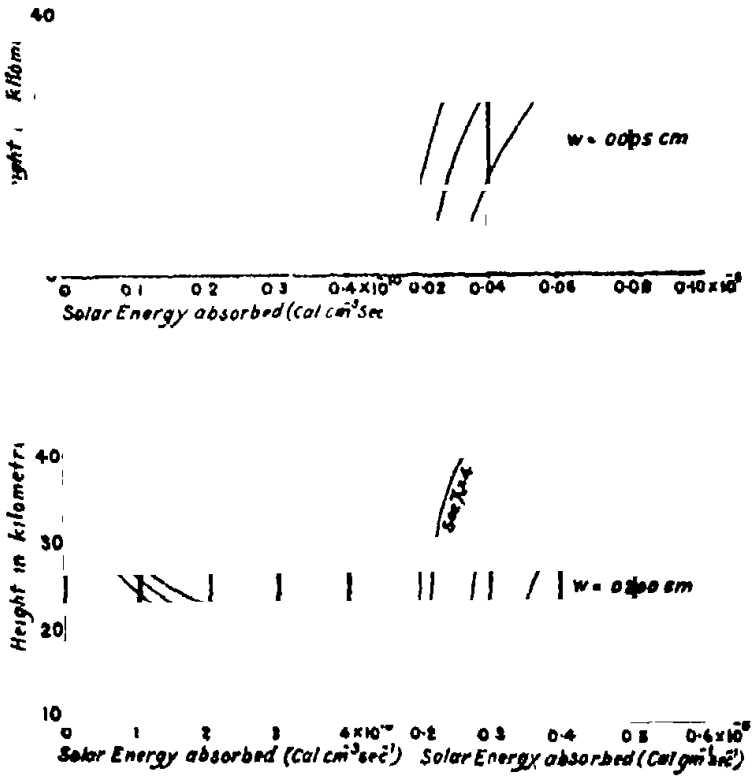

40
w = 0·05 cm
0 0·1 0·2 0·3 0·4×10⁻¹⁰ 0·02 0·04 0·06 0·08 0·10×10⁻⁸
Solar Energy absorbed (Cal cm⁻³ Sec
Height in kilometres
40
30
20
10
w = 0·05 cm
0 1 2 3 4×10⁻¹⁰ 0·2 0·3 0·4 0·5 0·6×10⁻⁸
Solar Energy absorbed (Cal cm⁻³ sec⁻¹) Solar Energy absorbed (Cal gm⁻¹ sec⁻¹)

FIG 11. Height distribution of the absorption of solar energy by water vapour W = total precip tab'e water above 16 km Relative humidity near 16 km is assumed to be 100% and the distribution of moisture in the stratosphere governed by Dalton's law

Recent measurements in Europe show that the stratosphere there is often surprisingly dry, dew points as low as — 80° C being obtained In the present paper, calculations are made for four different values of total precipitable water above the arbitrarily chosen reference level of 16 km., W = 0005.

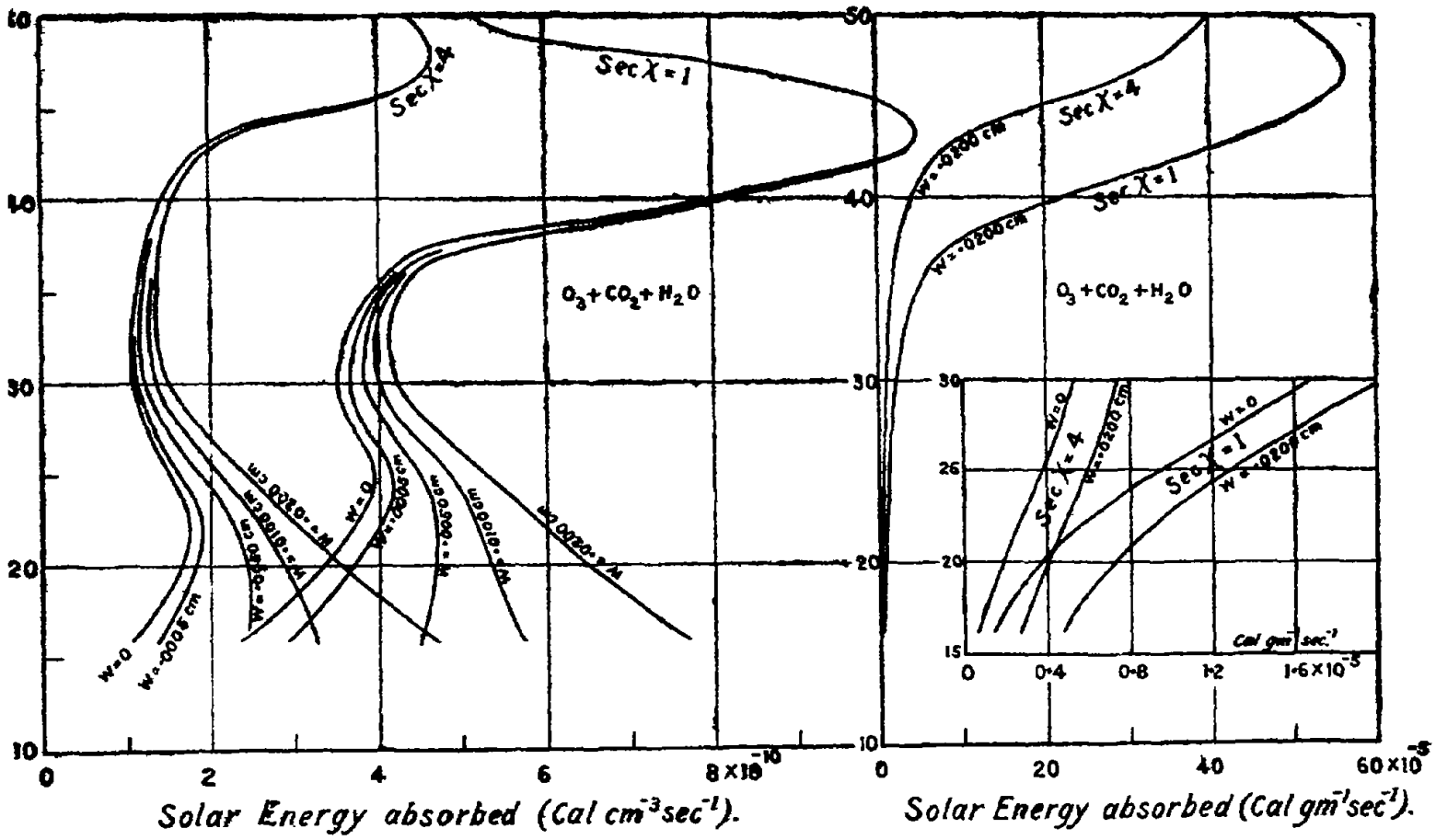

Sec χ = 4
Sec χ = 1
W = 0
W = 0·005 cm
W = 0·010 cm
W = 0·020 cm
W = 0·040 cm
W = 0·080 cm
W = 0·160 cm
W = 0·320 cm
$O_3 + CO_2 + H_2O$
Solar Energy absorbed (Cal $cm^{-3} sec^{-1}$).
Sec χ = 4
Sec χ = 1
W = 0·0200 cm
W = 0·0200 cm
$O_3 + CO_2 + H_2O$
W = 0
W = 0·0320 cm
W = 0·0160 cm
Cal gm^{-1} sec^{-1}
Solar Energy absorbed (Cal $gm^{-1} sec^{-1}$).

Fig. 12 Height distribution of the absorption of solar energy by (i) ozone (distribution at Tromsø for x = 0·260 cm) plus (ii) carbon dioxide (total CO_2 content = 240 cm.), plus (iii) water vapour (total ppt H_2O above 16 km = W cm.) Inset on the right-hand side gives the values of E_w below 30 km on a magnified scale.

005, ·010, 020 cm, the distribution in the stratosphere being given by Dalton's law. These values correspond to 100% relative humidity at the tropopause, the approximate saturation temperatures being $-80°$ C, $-65\ 5°$ C, $-60\ 5°$ C and $-55\ 5°$ C respectively. These results with suitable changes may be used for application to actual cases Fig. 11 gives the results for the two extreme values of W and for different values of sec χ.

(*d*) *The total effect*—Having obtained the separate contributions to solar energy absorption due to ozone, CO_2 and water vapour, the three may be suitably added Fig 12 gives the results for Tromsø with total ozone $x = 0\ 260$ cm, total CO_2 C = 240 cm, and different values of W. The mass density of energy absorption for ozone near 50 km is considerably larger than that due to water vapour and the curves for different values of W merge into each other Below 30 km, however, the two effects are comparable and the inset in Fig. 12 shows the results on an enlarged scale for two extreme values of W.

§ 7 Discussion of Results

Throughout the work, the calculations are made on the assumption that the quantity of ozone above 50 km is negligible The effect of this will be to reduce slightly the actual values of E_v and E_m in the first few layers. But as stated by Dobson, the ozone values above 45 km are only approximate and one cannot expect very accurate results for this region The error decreases rapidly as we go to the lower layers, and is practically zero below 40 km

Results similar to Fig. 9 were obtained also for the ozone distribution at Arosa and the general nature of the curves was found to be the same as that for Tromsø. The energy absorption near 50 km. level is large and it goes on decreasing as we approach the earth. This means that the small quantities of ozone present in the uppermost layers are mainly responsible for the absorption of large amounts of solar energy, the main ozone mass near its centre of gravity playing only a subsidiary part

Considering the mass density E_m of solar energy absorption, the region under consideration can be roughly divided into two parts. The contribution due to ozone predominates in the region 50 to 30 km, while below 30 km., the effect due to water vapour predominates The contribution due to CO_2 is small throughout the region.

In conclusion, the author wishes to express his grateful thanks to Diwan Bahadur Dr. K. R Ramanathan for his advice and interest throughout this work.

APPENDIX I

Values of the Absorption Coefficients and Other Constants Used in this Paper

(1) *Radiation and solar constants.*—

$C_1 = 3\ 703 \times 10^{-5}$ erg cm.$^{-2}$ sec^{-1}; $C_2 = 1\ 433$ cm °K.;

$\sigma = 5\ 709 \times 10^{-5}$ erg cm^{-2} sec^{-1} K.$^{-4}$;

1 erg cm.$^{-2}$ sec.$^{-1}$ $= 2\ 389 \times 10^{-8}$ cal cm^{-2} sec^{-1}

Solar Constant, S $= 2\ 045$ cal cm^{-2} min^{-1}

For the distribution of radiant energy, the temperature of the sun is assumed to be 6000° K

(2) *Ozone bands.*—

α = decimal absorption coefficient per cm of ozone measured at N.T.P. Only a few values of α read from the smoothed curves are given.

k_1 = generalized absorption coefficient per cm of ozone in the relation

Author	Ny Tsi Ze and Choong		A Tournaire—Vassy		Adel and Lampland		Hettner, Pohlmann and Schumacher	
Band	Hartley 2000–3300 Å		Chappuis 4400–7600 Å		9·6 μ		4·75 μ	14·1 μ
Pressure	Atmospheric		Atmospheric		25 mb.		25 mb.	25 mb
	λ in Å	α	λ in Å	α at 18° C	λ in μ	α	Average k	Average k
	2000	(1)	4400	001	9·3	04		
	2200	25	4800	·008	9·4	99		(*a*) Average for 12–13μ and 15·2–16·5μ, k = 0115
	2400	99·2	5200	025	9·46	1·45		
	2500	139	5600	·052	9·5	1·27	Average for the region 4·65–4·90μ, k=0·177	
	2563	145	6000	·065	9·56	·91		
	2600	138·5	6400	·038	9·6	1·11		
	2700	97·5	6800	·018	9·65	1·27		(*b*) Average for 13–15·2μ, k = ·093
	2900	19·8	7200	·005	9·7	1·15		
	3100	1·47	7600	·002	9·9	·54		
	3300	·065	..	.	10·1	06		

(3) *Carbon dioxide bands*—(*a*) α = decimal absorption coefficient per cm. of CO_2 at N.T.P.

Barker, 1922.				Martin and Barker, 1932
2·7 μ band				4·3 μ band
λ in μ	α	λ in μ	α	Average α
2·667	017	2·753	·073	(a) For 4 19 to 4·21 μ, α = 0·97
2 677	·089	2·767	025	(b) For 4 21 to 4 30 μ, α = 3·57
2·691	031	2 777	062	(c) For 4 30 to 4 37 μ, α = 1 18
2·698	089	2 80	·018	(d) Average for 4 19 to 4·37μ, α = 2·10
2·738	·011	2·81	·003	

(*b*) Callendar's empirical formula for CO_2 bands $A = 1 - (1 + nc^x)^{-1}$, where C = cm of CO_2 at N.T P.

Band	14–16 μ	13–14 μ and 16–17 μ	12·5–13 μ and 17–17 5 μ	9–11 μ
n ..	0 9	0·08	0·0055	0·00017
x	0·84	0 67	0·67	1

(4) *Water vapour bands.*—(*a*) Hettner's data used. α = decimal absorption coefficient per cm of ppt H_2O at N.T.P.

ρ (0 89–0·99 μ)	φ (1 08–1 19 μ)	ψ (1 27–1 53 μ)		Ω (1·70–2·02 μ)	
Average α	Average α	λ in μ	α	λ in μ	α
0·274	0 533	1 27	0	1·70	0
		1·30	0 55	1 75	0·43
		1 33	2 38	1·78	2 19
		1·35	6·50	1 80	5·15
		1·37	10·1	1 82	9 90
		1 40	6 89	1 86	12·6
		1·43	3·77	1·90	10·1
		1 45	1·88	1 94	5·46
		1 49	0 73	1 96	2·23
		1 53	0	2 00	0·37
		..	..	2 02	0·16

(*b*) Fowle's data for W = 0 008 cm. of ppt H_2O was used to calculate β in the relation $A = \phi(\sqrt{\beta}\ V)$.

Band	Range in μ	Observed % absorption	β
X_1 ..	2 2–3·2	23·6	5·6
X_2 .	3·2–4·0	21·7	4·7
Y ..	4 0–4·9	33·5	11·0
Z_1 ..	4·9–5·4	16	3·3
Z_2 .	5·4–5·9	47	24·7
Z_3 .	5·9–6·4	64	52·4
Z_4 .	6·4–7·0	62	61·5
Z_5 ..	7·0–8·0	25	6·3

APPENDIX II

Evaluation of the Band-Absorption of Radiation

The band absorption of radiation incident on a gaseous layer of thickness Z can be evaluated as follows, when the relation between the decimal absorption coefficient α and the wavelength λ has the form of the normal error equation, $\alpha = \alpha_0 e^{-h^2(\lambda-\lambda_0)^2}$, and the intensity of the incident radiation has the linear form $J_\lambda = k + m\lambda$. The energy absorption in the band within the limits λ_1 to λ_2, $(\lambda_1 < \lambda_0 < \lambda_2)$, is

$$E_r = \int_{\lambda_1}^{\lambda_2} J_\lambda \left(1 - e^{-Z\beta e^{-h^2(\lambda-\lambda_0)^2}}\right) d\lambda, \text{ where } \beta = 2\ 303\ \alpha_0$$

$$= \int_{\lambda_1-\lambda_0}^{\lambda_2-\lambda_0} [k + m(u+\lambda_0)] \left(1 - e^{-Z\beta e^{-h^2u^2}}\right) du, \text{ by putting } \lambda - \lambda_0 = u$$

$$= (k + m\lambda_0) \int_{\lambda_1-\lambda_0}^{\lambda_2-\lambda_0} \left(1 - e^{-\beta Z e^{-h^2u^2}}\right) du + m \int_{\lambda_1-\lambda_0}^{\lambda_2-\lambda_0} u \left(1 - e^{-\beta Z e^{-h^2u^2}}\right) du$$

Putting $p = \beta Z$ and $x = \beta Z e^{-h^2u^2} = pe^{-h^2u^2}$,

clearly $1 - e^{-\beta Z e^{-h^2u^2}} = 1 - e^{-x} = \sum_1^\infty (-1)^{n+1} \frac{x^n}{n!} = \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} e^{-nh^2u^2}$

$$E_r = (k + m\lambda_0) \int_{\lambda_1-\lambda_0}^{\lambda_2-\lambda_0} \left(\sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} e^{-nh^2u^2}\right) du$$

$$+ m \int_{\lambda_1-\lambda_0}^{\lambda_2-\lambda_0} \left(\sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} u e^{-nh^2u^2}\right) du.$$

$$= (k + m\lambda_0)\ I_1 + m\ I_2$$

The integrals I_1 and I_2 involving infinite series can be solved term by term as follows:—

$$I_1 = \int_{\sqrt{n}\,h(\lambda_1-\lambda_0)}^{\sqrt{n}\,h(\lambda_2-\lambda_0)} \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{1}{\sqrt{n}\,h} e^{-t^2} dt \text{ by putting } \sqrt{n}\,hu = t,$$

$$= \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{1}{\sqrt{n}\,h} \frac{\sqrt{\pi}}{2} \frac{2}{\sqrt{\pi}} \int_{\sqrt{n}\,h(\lambda_1-\lambda_0)}^{\sqrt{n}\,h(\lambda_2-\lambda_0)} e^{-t^2} dt$$

$$= \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{\sqrt{\pi}}{2\sqrt{n}\,h} \left[\frac{2}{\sqrt{\pi}} \int_{\sqrt{n}\,h(\lambda_1-\lambda_0)}^{0} e^{-t^2} dt + \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{n}\,h(\lambda_2-\lambda_0)} e^{-t^2} dt\right]$$

since $\lambda_1 < \lambda_0 < \lambda_2$, *i.e.*, $\lambda_1 - \lambda_0 < 0 < \lambda_2 - \lambda_0$

$$-\sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{\sqrt{\pi}}{2\sqrt{n}\,h} \left[\frac{2}{\sqrt{\pi}} \int_0^{\sqrt{n}\,h\,(\lambda_0-\lambda_1)} e^{-t^2}\,dt + \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{n}\,h\,(\lambda_2-\lambda_0)} e^{-t^2}\,dt\right]$$

$$= \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{\sqrt{\pi}}{2\sqrt{n}\,h} \left[\phi\left(\sqrt{n}\,h\,\overline{\lambda_0 - \lambda_1}\right) + \phi\left(\sqrt{n}\,h\,\overline{\lambda_2 - \lambda_0}\right)\right]$$

where ϕ denotes the well-known error function

Also, $I_2 = \int_{\lambda_1-\lambda_0}^{\lambda_2-\lambda_0} \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!}\, u\, e^{-nh^2u^2}\,du$

$$= \int_{nh^2(\lambda_1-\lambda_0)^2}^{nh^2(\lambda_2-\lambda_0)^2} \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{1}{2\sqrt{n}h^2} e^{-y}\,dy \qquad \text{by putting } nh^2u^2 = y$$

$$= \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{1}{2nh^2} \left[-e^{-y}\right]_{nh^2(\lambda_1-\lambda_0)^2}^{nh^2(\lambda_2-\lambda_0)^2}$$

$$= \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!} \frac{1}{2nh^2} \left[e^{-nh^2(\lambda_1-\lambda_0)^2} - e^{-nh^2(\lambda_2-\lambda_0)^2}\right]$$

$$E_r = (k + m\lambda_0) \frac{\sqrt{\pi}}{2h} \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!\sqrt{n}} \left[\phi\left(\sqrt{nh^2(\lambda_0-\lambda_1)^2}\right) + \phi\left(\sqrt{nh^2(\lambda_2-\lambda_0)^2}\right)\right]$$

$$+ \frac{m}{2h^2} \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!\,n} \left[e^{-nh^2(\lambda_1-\lambda_0)^2} - e^{-nh^2(\lambda_2-\lambda_0)^2}\right]$$

Putting $h^2(\lambda_1-\lambda_0)^2 = A$, $h^2(\lambda_2-\lambda_0)^2 = B$, and $k + m\lambda_0 = J_{\lambda_0}$,

$$E_r = J_{\lambda_0} \frac{\sqrt{\pi}}{2h} \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!\sqrt{n}} \left[\phi\left(\sqrt{nA}\right) + \phi\right. \qquad [1]$$

$$+ \frac{m}{2h^2} \sum_1^\infty (-1)^{n+1} \frac{p^n}{n!\,n} \left[e^{-nA} - e^{-nB}\right]$$

$$= J_{\lambda_0} \frac{\sqrt{\pi}}{2h} \cdot S_1 + \frac{m}{2h^2} S_2$$

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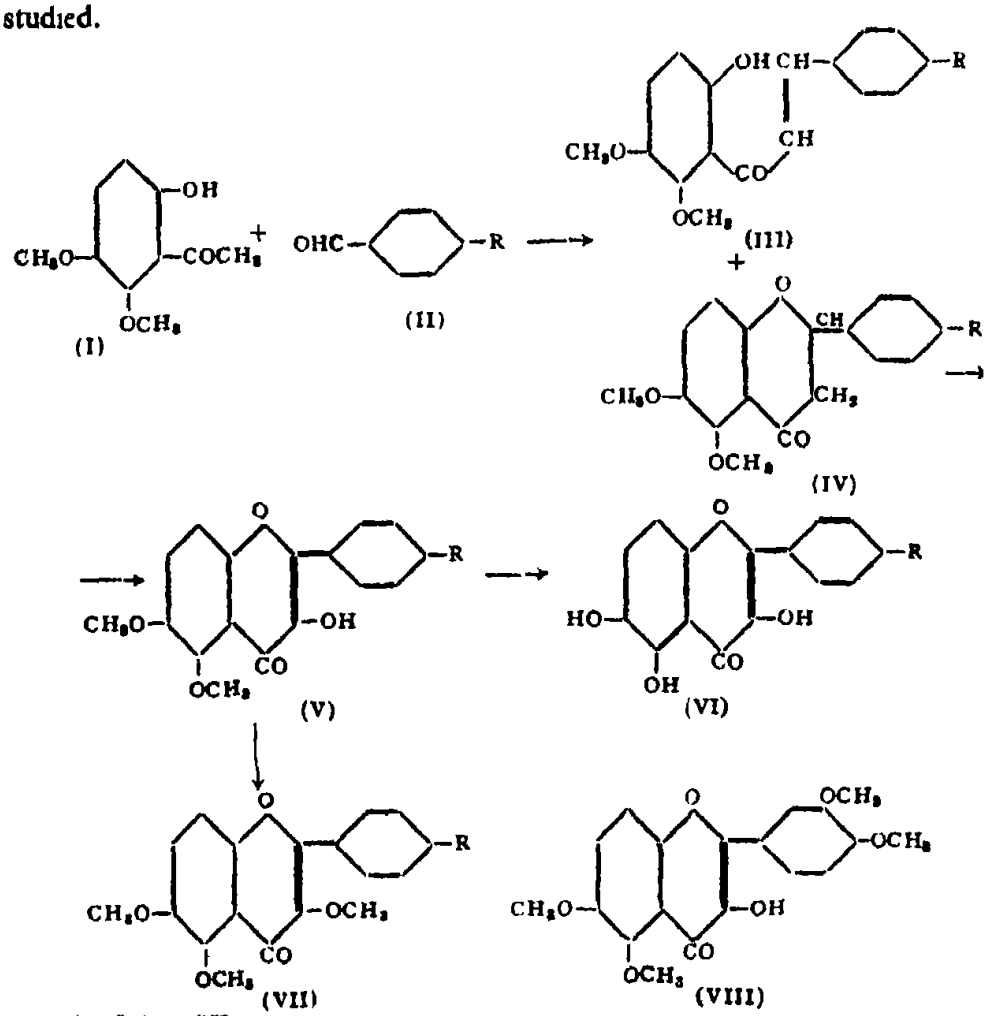
SYNTHESIS OF 5: 6-HYDROXY-FLAVONOLS
PART III

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IN Part II[1] the synthesis and study of 3 . 5 · 6 : 3′ : 4′-pentahydroxy-flavone and its derivatives were described. Following the same procedure the two lower members of this series have now been prepared and their properties studied.



R=H, OCH_3 or OH

Since in the chalkone condensation it is necessary to have the hydroxyl groups protected as far as possible in order to get good yields, 2-hydroxy-

5: 6-dimethoxy-acetophenone (I) was employed instead of the more easily available 2 5-dihydroxy ketone and the condensation made with benzaldehyde and anisaldehyde In each case the product was a mixture of both the chalkone and the corresponding flavanone Similar mixture resulted even when the chalkone was heated with alcoholic sulphuric acid The conversion of the flavanone into flavonol was effected directly in one stage since it gives better yields of the products

The 5: 6-hydroxy-flavonols described in the course of this work form a series of compounds lacking a hydroxyl group in the 7-position There is marked absence of fluorescence as compared with the 7-hydroxy and 5. 7-dihydroxy compounds The importance of the 7-position for this property is thus indicated They form brownish-red solutions in alkali which rapidly fade on shaking with air This characteristic seems to be also due to the presence of two hydroxyl groups in the contiguous positions 5 and 6

The compounds of type (V) having only a hydroxyl group in the 3-position exhibit fluorescence in alcoholic solutions but not in strong sulphuric acid. They also give prominent ferric chloride colour The fully methylated compounds (type VII) also give some fluorescence in alcohol but none in sulphuric acid

The possibility of the flavone ring opening and reclosing in a different direction, during demethylation using boiling hydriodic acid, has been shown to be present in the case of the 5 8-hydroxy flavones.[8] No definite example is known of 5. 6-hydroxy compounds changing in this manner This point has been examined in one typical case in the course of the present work. 3-Hydroxy-5. 6: 3'. 4'-tetra-methoxy-flavone (VIII), was demethylated to the pentahydroxy compound which was again remethylated with dimethyl sulphate and potassium carbonate in acetone solution The product was found to be identical with that of direct methylation of (VIII) thus showing that no isomeric change is involved during the demethylation

Experimental

2-Hydroxy-5'6-dimethoxy-chalkone.—To a solution of 2-hydroxy-5: 6-dimethoxy-acetophenone (3 g.) and benzaldehyde (5 c c) in alcohol (20 c.c) cooled to 0°, potassium hydroxide (30 g. in 24 c.c of water) was added in small quantities at a time with shaking After the addition, the flask was stoppered tight and kept for four days at the laboratory temperature with occasional shaking. The contents were then diluted with water and ether-extracted in order to remove the unreacted aldehyde and then acidified The product separated in the form of an orange-red liquid which was taken in ether The ethereal solution was shaken with aqueous sodium bicarbonate

to remove benzoic acid that was also formed during the reaction On evaporating the ether, a red liquid was obtained which did not solidify even after keeping in the refrigerator for a number of days The chalkone was soluble in alkali and gave a reddish brown colour with ferric chloride in alcoholic solution Crystallisation of the product was attempted using benzene, petrol, alcohol and acetone, but in all cases the chalkone was recovered as a liquid It was therefore directly employed for conversion into the flavanone.

In another experiment, the alkaline solution left after removing the unreacted aldehyde by means of ether, was saturated with carbon dioxide in the hope of obtaining the chalkone in a crystalline condition. A pale brownish yellow solid separated out (0 2 g) When crystallised from alcohol using animal charcoal, it came out in the form of colourless silky needles melting at 142–44° It did not depress the melting point of the flavanone obtained from 2-hydroxy-5 6-dimethoxy chalkone The filtrate from the flavanone on ether-extraction yielded the chalkone in the form of a viscous red liquid

5·6-*Dimethoxy-flavanone.*—A solution of the above chalkone (2 g.) in 50% aqueous alcohol (100 c c) was treated with concentrated sulphuric acid (3 c c.) and the resulting solution boiled under reflux for 24 hours. On concentrating the solution, the flavanone separated out in the form of pale yellow silky needles It was filtered and washed with water The adhering chalkone was removed by macerating the solid with a weak solution of sodium hydroxide It then crystallised from alcohol (animal charcoal) in the form of colourless silky needles melting at 142–44° (Found: C, 71 9, H, 5 8; $C_{17}H_{16}O_4$ requires C, 71 8; and H, 5 6%)

5:6-*Dimethoxy-3-hydroxy-flavone* —To a gently boiling solution of 5·6-dimethoxy-flavanone (0 5 g) in alcohol (40 c c.) were added alternately amyl nitrite (3 c c) and concentrated hydrochloric acid (20 c c ; d , 1 19) little by little with stirring After the addition, the contents were left for two hours with occasional shaking The solution was then diluted with water (150 c.c) and the solid product filtered and washed with water It was crystallised twice from alcohol when the flavonol was obtained as rhombic plates, melting at 216° Yield, 0·15 g. It gave a reddish brown colour with alcoholic ferric chloride When reduced in alcoholic solution with magnesium and hydrochloric acid an orange-red colour was developed. It was soluble in aqueous alkali to give an yellow solution. An alcoholic solution of the flavonol exhibited green fluorescence It dissolved in concentrated sulphuric acid to yield a yellow solution without fluorescence (Found: C, 68·5; H, 4·7. $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%).

3·5·6-*Trihydroxy-flavone.*—The above dimethoxy flavonol (75 mg.) dissolved in acetic anhydride (3 c c) was treated with hydriodic acid (2 c.c.; d., 1·7) with cooling. The solution was refluxed for an hour in an oil-bath kept at 150–55°. After cooling, it was treated with sulphurous acid when a pale yellow crystalline solid separated out The aqueous solution along with the solid was ether-extracted On removing ether a pale yellow crystalline solid was obtained It was crystallised from ethyl acetate when the dihydroxy flavonol came out as stout rectangular rods melting at 183–85° Yield, 50 mg It gave a brown ferric chloride colour and exhibited no fluorescence either in concentrated sulphuric acid or in alcoholic solution. It was insoluble in sodium bicarbonate and carbonate solutions but dissolved in aqueous sodium hydroxide to form a brownish red solution; the colour faded slowly to pale yellow, the change being very fast on shaking with air (Found: C, 67 0; H, 3 7, $C_{18}H_{16}O_8$ requires C, 66·7 and H, 3·7%)

3:5·6-*Trimethoxy-flavone.*—To the above dihydroxy flavonol (40 mg) in anhydrous acetone (20 c c) was added anhydrous potassium carbonate (0·5 g.) and dimethyl sulphate (0 2 c c) and the mixture refluxed for 20 hours. The solvent was removed and water added when a very pale yellow solid separated This was filtered, washed with water and crystallised from benzene-petrol mixture when the trimethyl ether came out as stout rhombohedral prisms melting at 130–32°. It gave no ferric chloride colour in alcoholic solution It exhibited no fluorescence either in alcohol or in sulphuric acid solution (Found: C, 69·4; H, 4 8, $C_{18}H_{16}O_8$ requires C, 69·2; H, 5·1%).

5:6:4'-*Trimethoxy-3-hydroxy-flavone* —This compound was obtained from the corresponding flavanone[8] in one operation as in the previous case

The colourless solution of the flavanone (0 5 g.) in alcohol (40 c.c.) gradually turned reddish orange on treatment with amyl nitrite (3 c.c.) and concentrated hydrochloric acid (30 c.c., d., 1·19). After 2 hours, the liquid was diluted to 200 c.c with water. Pale yellow shining flakes separated out after some hours. They were collected and crystallised twice from alcohol The flavonol was obtained in the form of pale yellow broad rectangular plates melting at 172–73° Yield, 0·15 g. It gave bright bluish green fluorescence in alcohol, benzene and ether solutions With alcoholic ferric chloride a light brown colour was obtained. It was sparingly soluble in cold aqueous sodium hydroxide yielding a very pale yellow solution. In concentrated sulphuric acid it dissolved forming an orange coloured liquid with no fluorescence (Found· C, 65·8; H, 5·1; $C_{18}H_{16}O_8$ requires C, 65·9; and H, 4·9%).

3 : 5 : 6 : 4'-*Tetramethoxy-flavone.*—The trimethoxy flavonol (0·1 g.) was methylated by refluxing it in a solution of anhydrous acetone (50 c.c) with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.) for 8 hours. At the end of the reaction, the potassium salts were filtered and washed with warm acetone. The filtrate was concentrated on the water-bath (2 c.c.) and treated with water (2–3 c.c.). The semi-solid precipitate did not crystallise even ater keeping for a long time in the ice-chest. It was, therefore, extracted with ether and the residue obtained after the removal of ether was crystallised twice from alcohol when it was obtained as colourless rectangular plates melting at 147–48°. It gave no colour with ferric chloride in alcoholic solution. Its solution in alcohol exhibited bluish green fluorescence. However, fluorescence was absent in concentrated sulphuric acid (Found: OCH_3, 36 0, $C_{19}H_{18}O_6$ requires OCH_3, 36·3%)

3 : 5 : 6 . 4'-*Tetrahydroxy-flavone* —A solution of 5 : 6 : 4'-trimethoxy-3-hydroxy-flavone (0·2 g.) in acetic anhydride was treated with hydriodic acid (d., 1·7; 5 c.c. with cooling) The resulting solution was refluxed on an oil-bath at 150–55° for 2 hours. It was diluted with water and saturated with sulphur dioxide when an orange coloured precipitate was obtained. When crystallised twice from ethyl acetate, the trihydroxy flavonol was obtained in the form of pale yellow microscopic crystals melting at 305° with slight sintering at 294° Yield, 0·1 g With alcoholic ferric chloride a dark olive green colour was obtained It exhibited no fluorescence either in alcoholic or in strong sulphuric acid solution It was insoluble in aqueous sodium bicarbonate, but dissolved in carbonate solution giving a fairly stable pale yellow colour In aqueous sodium hydroxide it formed a brownish red solution which faded slowly to pale brownish yellow; the change was very rapid when shaken with air. It did not show marked colour changes in alkaline buffer solutions; in a solution of pH 12·2, it was bright yellow at first, rapidly turning brown; within 4 minutes it was deep brown, after an hour reddish brown and after 24 hours pale reddish brown (Found C, 62·8; H, 3·8; $C_{15}H_{10}O_6$ requires C, 62·9, and H, 3·5%)

Summary

The synthesis of 3 5 6· 3' 4'-pentahydroxy-flavone was already reported The lower members of this group of 5 6-hydroxy flavonols with one and no hydroxyl group in the side-phenyl nucleus have now been prepared by Kostanecki's method The characteristic properties are described.

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EVIDENCE FOR THE EXISTENCE OF THE "EMISSION LAYER" IN THE ATMOSPHERE

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1. Introduction

The vertical distribution of temperature in the atmosphere is a factor of great importance in determining the processes of weather. Results of upper air soundings all over the world have shown that broadly the atmosphere can be divided into two thermally distinct zones. In the lower zone, known as the *troposphere*, the temperature decreases steadily with height at the rate of approximately 6° C /km. In the upper region, known as the *stratosphere*, the temperature remains constant or increases slightly with height. The surface of separation between the troposphere and the stratosphere is known as the *tropopause*. The tropopause is approximately 18 km. above the ground at the Equator, about 12 km high in middle latitudes and 8 km high at the poles A problem of fundamental importance in Meteorology, which is as yet not completely solved, is to find out a rational physical explanation for the observed distribution of temperature in the atmosphere.

2 Solar and Terrestrial Radiation

In any attempt to answer this question, we have to start from the fundamental fact that the ultimate source of energy for all atmospheric phenomena is the solar radiation intercepted by the earth and its atmosphere. Since the mean temperature of the system (earth + atmosphere) does not show any appreciable change over long intervals of time, it follows that as much energy is sent back to outer space by this system as is received by it.

There is, however, an essential difference in the spectral characteristics of the incoming and outgoing streams of radiant energy. The solar radiation corresponds approximately to black body radiation at a temperature of 6000 °A; practically the entire energy is confined between the wave-length limits $\lambda = 0.15\mu$ to $\lambda = 4\mu$ with peak intensity at $\lambda_m = 0.5\mu$. As contrasted with this, the energy of terrestrial radiation is spread out over the band of wave-lengths from about 3μ to 120μ with peak intensity at about 10μ to 15μ, corresponding to black body radiation at a temperature of 200 to 300 °A We may, therefore, picture the earth and its atmosphere as constituting a system which is continually absorbing short-wave solar radiation and radiating it back into space in the form of long-wave heat radiation,

3. Radiative Equilibrium

If the entire solar energy reaching the outer surface of the earth's atmosphere passes through without any depletion due to reflection and scattering, then every sq cm of the earth's surface would receive on the mean during the day and night 0 5 cal /min Under radiative equilibrium, therefore, the same amount of energy should be radiated out by each square cm of the earth's surface Assuming that the surface radiates like a black body, the mean temperature T is given by.

$$\sigma T^4 = 0\ 5 \text{ cal /cm.}^2 \text{ min}$$

where $\sigma = 5\ 73 \times 10^{-5}$ erg cm^{-2} deg^{-4} sec^{-1} (Stefan's constant)

This equation when solved for T gives

$$T = 279\ ^\circ A = +6^\circ C \qquad (1)$$

We know, however, that about 40% of the incoming solar energy is directly returned to space due to reflection, scattering, etc If it is assumed that the remaining 60% is absorbed at the surface of the earth, then the corresponding equation for radiative equilibrium becomes

$$\sigma T^4 = 0{\cdot}3 \text{ cal /cm}^2 \cdot \text{min}$$

which gives

$$T = 246\ ^\circ A = -27^\circ C \qquad (2)$$

The observed mean temperature of the earth's surface is however $+14^\circ C$, *i e*, it is higher than either of the above values.

4 "Glass House Effect" of the Atmosphere

What is the reason for this high surface temperature of the earth? In order to understand this, we have to consider the assumptions on which the calculations in the preceding section were based. We tacitly assumed that the atmosphere is perfectly transparent to both solar and terrestrial radiation so that the incoming and outgoing streams of radiant energy pass through the atmosphere without any attenuation We know, however, that while the atmosphere is largely transparent to short-wave solar radiation, it is highly opaque to wave-lengths in the range of terrestrial radiation, because the water vapour and CO_2 always present in the atmosphere possess intense absorption bands in this spectral region. Consequently, the greater part of the heat radiation from the earth's surface is absorbed and trapped by the water vapour and CO_2 in the lowest layers of the atmosphere These constituents in their turn re-radiate energy over the same wave-lengths at which they absorb, so that a downward stream of radiant energy is directed toward the surface of the earth from the lower layers of the atmosphere (Gegen-

strahlung). The net loss of energy from the surface of the earth (Ausstrahlung) is now less than before; it is equal to the difference between σT^4 and the Gegenstrahlung Thus the effect of water vapour and CO_2 is to reduce the loss of heat from the surface of the earth or to increase the surface temperature This is known as the "Glass House Effect" of the atmosphere.

5 Radiative Loss of Heat from the Atmosphere and Albrecht's Emission Layer

With an atmosphere which absorbs and radiates like a black body, the net loss of heat from the earth's surface would be reduced practically to zero, because all the radiation sent out from the earth will be absorbed in the lowermost layers which have practically the same temperature as the earth and would therefore send back an equal amount of radiation towards the earth. However, the water vapour and CO_2 which constitute the major absorbing and radiating constituents of the lower atmosphere do not absorb all wavelengths in the range of terrestrial radiation As was first shown by Simpson, the absorption spectrum of water vapour in this spectral region can be broadly divided into three categories.—

(1) The spectral band $8\frac{1}{2}\mu$ to 11μ in which water vapour is completely transparent

(2) The bands 7μ to $8\frac{1}{2}\mu$ and 11μ to 14μ in which water vapour is semi-transparent

(3) Wave lengths $< 7\mu$ and $> 14\mu$ for which water vapour is so highly opaque that a small amount (according to Simpson 0·3 mm of precipitable water) is sufficient to absorb completely all radiation

Out of the total energy σT^4 radiated from the surface of the earth, the entire amount comprised in the spectral band (1) and a portion of the energy in the spectral range (2) are thus directly lost to outer space. It is estimated that out of the 60% incoming solar energy absorbed by the earth and the atmosphere, about 10% only is disposed of in this way. The remaining 50% of long-wave heat radiation returned to space is contributed by the atmosphere.

From which part of the atmosphere does this large amount of heat radiation which is being continually lost to outer space originate? This is a most important problem in the theory of atmospheric heat radiation. We have seen that the principal absorbing and radiating constituents of the lower atmosphere are water vapour and to a lesser extent CO_2. These constituents, however send out radiation over the same wave-lengths at

which they absorb intensely If we now picture the atmosphere as being divided into a number of layers each of which contains the optimum quantity of the absorbing constituents to intercept completely the radiation from the layer below it, then, it is easy to see that outward radiation to space can begin only at such a height above which the amount of water vapour and CO_2 present is insufficient to absorb completely all the radiant energy arriving from below

Simpson assumed that the stratosphere contains enough water vapour to absorb all the radiation coming from the troposphere and that outward radiation to space from the atmosphere originates only from the stratosphere Later work has, however shown that Simpson's assumption requires revision.

From a careful study of the absorption and emission spectrum of water vapour, F Albrecht came to the conclusion that the greater part of the heat radiation sent out into space from the earth's atmosphere has its origin in the upper troposphere and that this radiation passes through the stratosphere without appreciable depletion According to Albrecht, radiation to outer space from a cloud-free atmosphere is mostly from a layer of about 3 to 4 km thickness in the upper troposphere, which he designated as the "*Emission Layer*" The radiation from the emission layer is independent of geographical latitude or of the time of the year and is approximately equal to the selective radiation of water vapour and CO_2 at a temperature of $-50°$ C

The location of the emission layer in the atmosphere is determined by two important considerations, *viz*.

(1) It contains an optimum amount of water vapour and CO_2 (the constituents that give rise to emission).

(2) The amount of water vapour and CO_2 above the layer is so small that the radiation from the emission layer passes through without appreciable attenuation

As the emission layer is a region which is losing heat throughout day and night, it is also a part of the atmosphere which is getting continually cooled due to this heat loss

According to Albrecht's estimates, the emission layer is located at such a height that the water vapour content at its base is approximately 0·1 gm./m^3 and its top 01 gm /m^3 Consequently, the height of the emission layer varies with the temperature and humidity content of the atmosphere. It has been estimated by Albrecht that when the atmosphere is hot and humid, the emission layer should lie roughly between the levels corresponding to 233 °A and 213 °A, when the atmosphere is comparatively dry, the emission layer should extend from 243 °A to 223 °A.

More recent researches on the absorption spectrum of water vapour have shown that the absorption coefficients given by the earlier workers are far too high and hence would necessitate a much higher value than what Simpson assumed for the critical quantity of precipitable water which constitutes a " black body " for the range of wave-lengths over which water vapour shows marked absorption Brunt has pointed out that this would not essentially modify the arguments of Simpson and Albrecht although the base of the emission layer would be lower and its thickness more than what was estimated by Albrecht

6 Emission Layer and Tropopause

According to Albrecht, the top of the emission layer marks the upper limit of the troposphere in polar and temperate latitudes. In the tropics, however, on account of the strong penetrative convection from below, brought about mainly through the agency of water vapour, the tropopause is carried a few kilometres above the top of the emission layer As a result of this, the temperature of the upper troposphere (above the top of the emission layer and below the tropopause) in the tropics is *lowered* below what it would normally have been as a result of purely radiative processes. Hence, in radiative heat exchange with the lower layers of the stratosphere the upper levels of the tropical troposphere absorb more heat than they radiate out This is supposed to be the reason (perhaps only one of the reasons) for the sharp inversion at the tropopause and the rapid increase of temperature in the first few kilometres above that in the tropical stratosphere, a feature which is not observed in higher latitudes where the lower stratosphere is practically an isothermal region.

7. Distribution of Heat and Cold Sources in the Atmosphere

While the long-wave outgoing radiation from the atmosphere causes a perpetual cooling of the upper troposphere, practically all the addition of heat resulting from the absorption of short-wave solar radiation takes place essentially at the surface of the earth and in the lower layers near the surface Thus vertical temperature gradients are set up in the troposphere which give rise to vertical displacements of air masses when the gradients exceed the limits of stability Consequently, in spite of the continuous loss of heat from the top and addition of heat at the bottom, a dynamical equilibrium with certain limiting temperatures is established.

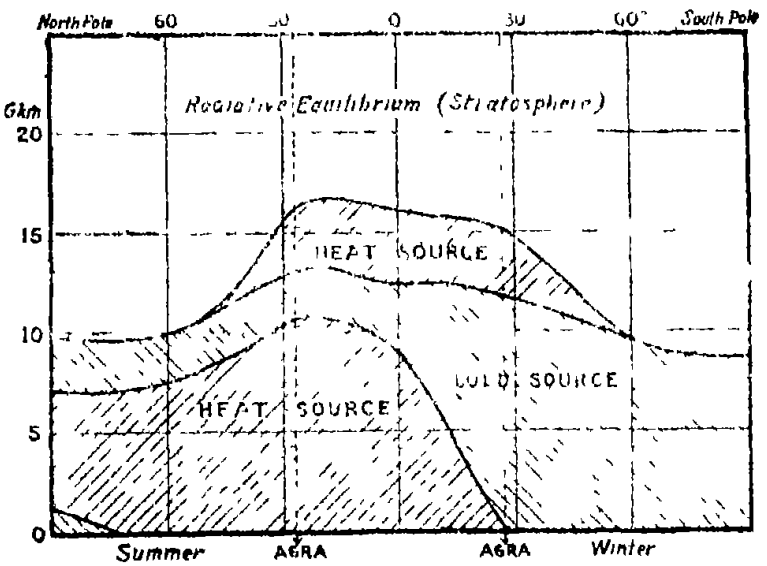
If we consider the annual mean heat balance of the system (earth + atmosphere), then according to Albrecht's calculations the incoming energy exceeds the outgoing up to latitude 37½°, while at higher latitudes the reverse conditions obtain. As is well known, it is this peculiar latitudinal distri-

bution of incoming and outgoing energy that brings about the general circulation of the atmosphere

Bjerknes has divided the troposphere into regions where there is a net gain of heat or a net loss of heat The former are called heat sources and the latter cold sources The principal cold source in the atmosphere is Albrecht's emission layer which is continually sending out heat energy into outer space The principal heat source is the lower troposphere in the tropics and the adjoining temperate latitudes which gains a net excess of energy in radiative heat exchange with the earth's surface and also in the form of latent heat of condensation Besides this, there is a secondary heat source which is the region comprised between the top of Albrecht's emission layer and the tropopause over the tropics and adjoining temperate latitudes This is a region which is cooled by convection below its radiative equilibrium temperature and as such gets a net excess of heat by radiative exchange with the lower layers of the stratosphere

8. Seasonal Variation of Heat and Cold Sources over the Northern Hemisphere

If we consider the vertical distribution of heat and cold sources over the northern hemisphere (Fig 1), there is a striking difference in the conditions which obtain in the summer and in the winter seasons. In the *northern*



PROBABLE SPATIAL DISTRIBUTION OF HEAT AND COLD SOURCES IN THE ATMOSPHER IN JUNE

(After Bjerknes)

Fig 1

summer, practically the whole of the lower troposphere is a heat source; the middle or the upper troposphere (Albrecht's emission layer) forms the cold source Above this lies the secondary heat source extending from the Equator up to and somewhat beyond 30° N In the *northern winter*, the lower heat source is displaced towards the southern hemisphere so that the entire troposphere (limited by the top of Albrecht's emission layer) over polar and temperate latitudes is a cold source suffering a continual loss of heat energy Above the top of this is a feeble heat source which stretches over a part of the temperate latitudes and is in fact an extension of the secondary heat source over the tropics brought about by meridional advection of air

9 Expected Seasonal Variations in the Thermal Structure of the Atmosphere over Temperate Latitudes Adjoining the Tropics

The considerations of the preceding section would lead us to expect striking seasonal variations in the thermal structure of the atmosphere over a place in the temperate latitudes adjoining the tropics Such observed variations in their turn can also be regarded as a proof of the general validity of the theoretical considerations outlined in the preceding sections and hence of the existence of the emission layer in the upper troposphere

What are the changes that we should expect in the thermal structure of the atmosphere over a place such as Agra (lat 27° 08′ long 78° 01′) between summer (July) and winter (January)?

Let us first consider the location of the cold source (Albrecht's emission layer) in these two months (see Fig 1) In July, the atmosphere is hot and humid and the emission layer (following Albrecht) may be taken to be between 11 to 14 gkm. In winter, the entire troposphere below the emission layer is a cold source; the emission layer itself should be between 8 and 11 km. according to the temperate limits given by Albrecht

In summer, the lower troposphere is a powerful heat source and the condensation of water vapour is by far the most important agency controlling the lapse-rates in the middle and upper troposphere. The lapse-rates at these levels would, therefore, follow the saturation adiabat which, however, is practically parallel to the dry adiabat under the conditions prevailing in the upper troposphere Within the emission layer itself, there is a continual cooling due to radiation, so that as a result of addition of heat at the bottom and loss of heat from the top there should be a marked tendency for super-adiabatic lapse-rates at these levels. Above the top of the

emission layer, convection and radiation work in opposite directions, the former tending to set up dry adiabatic lapse-rate while the latter tends to establish isothermal conditions Consequently a rapid decrease of lapse-rate with height should be noticed in the column above the top of the emission layer and below the tropopause The inversion at the tropopause would be very pronounced and a rapid rise of temperature with height should be the feature in the first few kilometres of the lower stratosphere

In the winter months, the entire troposphere below the top of the emission layer is a cold source undergoing continual cooling due to radiation The cooling increases with height and attains a maximum value within the emission layer The vertical distribution of lapse-rate should thus correspond to what would be expected in an air column which is continually cooled at the top, that is, the highest lapse-rates should occur in and below the emission layer Above the top of the emission layer, radiative processes alone would set up isothermal conditions However, meridional movement of air from lower towards higher latitudes transports the characteristics of the tropical tropopause to the temperate latitudes in a less pronounced form We should thus expect a "composite" type of tropopause over temperate latitudes, the transition from the troposphere to the stratosphere occurring in two stages The lower transition will correspond to the top of the emission layer, while the upper transition will correspond to the tropopause over the tropics. However, because of the absence of penetrative convection from below, the control by radiation will be more pronounced than in the tropics so that the lapse-rates and upper inversion above the top of the emission layer will be less conspicuous than in the tropics

In this connection it is interesting to recall a scheme of air circulation between the troposphere and the stratosphere which was suggested by Refsdal some years ago This is based on the work of Albrecht as well as on the concept originally put forth by Palmén that the tropopause should be regarded as a layer of transition which can dissolve at one level and reappear at a new level in the atmosphere depending upon dynamic as well as radiative conditions. In the temperate latitudes, the tropopause is dynamically sucked down in association with depressions and reforms at its original level when the depression activity has ceased. In this process, therefore, air from the stratosphere is transferred to the troposphere. According to Refsdal, the compensating transport of air from the troposphere to the stratosphere takes place in the tropics where the tropopause is carried above the top of the emission layer by convection, and consequently is constantly striving to build itself at a lower level under the influence of radiation.

From what we have discussed in the preceding, it would appear that the meridional movement of air from lower towards higher latitudes in the upper troposphere furnishes the necessary mechanism for the transport of air from the troposphere to the stratosphere; for, in the absence of penetrative convection from below at the higher latitudes, the high vertical temperature gradients which prevail in the upper levels of the tropical troposphere can no longer be maintained as the air moves over to the higher latitudes The lapse-rates would, therefore, progressively decrease in the meridionally advancing air column until finally it gets merged with the stratosphere in the higher latitudes The "composite" tropopause encountered in temperate latitudes appears to mark an intermediate stage in the transition of tropical tropospheric air into stratospheric air of the temperate latitudes.

10 Thermal Structure of the Atmosphere over Agra

A detailed study of the thermal structure of the atmosphere over Agra based on the results of over 500 sounding balloon ascents shows that the observed seasonal variations in the thermal structure of the atmosphere are quite in conformity with what should be expected in the light of Albrecht's work A detailed account of the investigation is being published elsewhere Some of the major features brought out by the study might, however, be summarised here:—

(1) In the month of July, the observed lapse-rates in the middle and upper troposphere over Agra practically follow the saturation adiabatic; super-adiabatic lapse-rates are frequently encountered between 12 and 14 gkm. Above 14 gkm , the lapse-rate begins to decrease and changes over into an inversion at about 18 gkm.

(2) Following the retreat of the monsoon in September, there is a decrease of lapse-rate in the upper troposphere and an increase in the middle troposphere over Agra

(3) A sudden decrease of lapse-rate at about 11 gkm. is noticed in a more or less conspicuous form during all the winter months

(4) The highest lapse-rates in the winter months are noticed between 7 and 11 gkm

(5) In the winter months, lapse-rates above 11 gkm. are generally feeble and gradually change over to an inversion at about 17 gkm

(6) The annual range of temperature in the atmosphere over Agra shows two maxima, one at about 9 gkm. and another at about 18 gkm. (see Fig. 2). Starting with the thermal conditions obtaining in summer

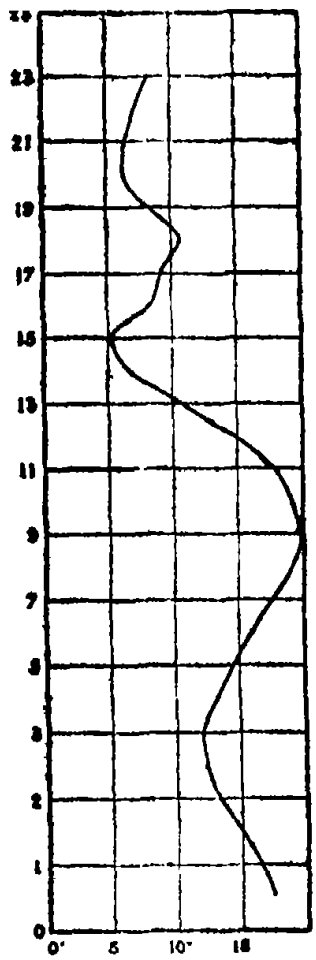


FIG. 2

(July), the lower maximum can be interpreted as the level of maximum cooling in winter (centre of gravity of the emission layer in this season) The upper maximum corresponds to the summer tropopause and is the region where the greatest fall of temperature below that corresponding to radiative equilibrium has been brought about by convection from below It follows that with decreasing control by convection and increasing control by radiation (transition from the monsoon to winter conditions), there should be a rise of temperature at all levels in the upper troposphere (above the top of the emission layer) and lower stratosphere, the rise of temperature being a maximum at the level of the summer tropopause,

All these facts lend strong evidence for the existence of the "Emission Layer" in the upper troposphere and the seasonal variation of its altitude depending upon the moisture content of the atmosphere.

11 Effect of Ozone Absorption on the Temperature of the Lower Stratosphere

Above the level of the tropopause, vertical transport of heat by convection is not possible, because of the extreme stability of the thermal stratification. Hence the temperature of the lower stratosphere should be conditioned mainly by the balance between absorbed and emitted radiation In addition to the part played by water vapour and CO_2 at these levels, the absorption and emission by ozone whose average height has been estimated to be between 20 and 25 km has no doubt to be taken into account in considering the radiative equilibrium of the lower stratosphere. Ozone has a strong absorption band between $0{\cdot}22\,\mu$ and $0\ 33\,\mu$ wherein the incoming solar radiation has appreciable energy. Probably about 5% of the incoming short-wave radiation is absorbed by ozone Again, ozone has another absorption band in the infra-red at $9{\cdot}5\,\mu$ It is significant that this band is close to the wave-length of maximum energy in terrestrial radiation, while water vapour is transparent for radiation of the same wave-length A detailed discussion of radiative phenomena in the stratosphere is unfortunately not yet possible because of gaps in our existing knowledge regarding the absorption spectrum of water vapour under stratospheric conditions as well as of the water vapour content of the stratosphere

Summary

The theory of radiative equilibrium demands that on the average the total amount of energy absorbed by the earth and its atmosphere in the form of short-wave solar radiation should be exactly equal to the total amount of energy given back to space in the form of long-wave heat radiation. From a study of the absorbing and radiating properties of the atmosphere, F. Albrecht arrived at the fundamental result that the major contribution to the long-wave heat radiation into outer space originates from a layer of some three to four kilometres thickness in the upper troposphere, which he designates as the "*Emission Layer*". The emission layer is thus a portion of the upper atmosphere which is continually cooling due to radiative loss of heat The height of the emission layer is a function of the water vapour content of the atmosphere; it is more when the atmosphere is hot and humid and less when the atmosphere is cold and dry.

The author has made a detailed study of the thermal structure of the atmosphere over Agra based on the results of sounding balloon ascents over a period of ten years. A number of interesting features find a ready explanation on the assumption that the emission layer over Agra is located approximately between 11 and 14 gkm. in the monsoon months and between 8 and 11 gkm. during the remaining months,—an assumption in conformity with Albrecht's work. The observed seasonal variations in the thermal structure of the atmosphere over Agra thus lend strong evidence for the existence of the emission layer in the atmosphere and the variation of its altitude depending upon the moisture content of the atmosphere

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MEASUREMENT OF THE TOTAL PRECIPITABLE WATER IN THE ATMOSPHERE ABOVE POONA BY MEASUREMENTS OF ABSORPTION IN THE NEAR INFRA-RED

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1 Introduction

A knowledge of the quantity of water vapour present at any moment in different air layers of the atmosphere above a station is of fundamental importance to the meteorologist. The humidity records obtained from sounding-balloon meteorographs sent up in the atmosphere give some indication of the variation of humidity with height; but the use of the hair element for the measurement of humidity has not been found to be quite satisfactory. The problem of improving the method of recording humidity is engaging the attention of many workers.

The possibility of estimating the total precipitable water in the atmosphere by a spectroscopic method was first demonstrated by Fowle[1] by using his laboratory measurements of the absorption coefficients of water vapour in the bands in the near infra-red. The spectroscopic method does not indicate the distribution of water vapour with height, but does provide a rapid means of estimating the total water content of the atmosphere above a station whenever the sun is not obscured by clouds. The method has been used by a number of workers.[2,3,4,5] The necessary apparatus was set up at Poona towards the end of 1939, and some measurements recorded in 1940. During 1941 the measurements were made regularly and the data obtained are discussed here. A description of the experimental arrangement, the method of taking the records and some typical results are given in the following sections.

2. Apparatus and Method of Observation

The apparatus (see Fig. 1) consists of:—

(1) a locally constructed spectrograph, L_1 and L_2 being the collimating and focussing lenses respectively and P a flint glass prism (an equilateral one) with base 7·8 cm. and hight 4 cm.;

(ii) an ordinary heliostat H with a front silvered mirror, to direct the sun's rays into the slit S of the spectroscope after being condensed by the lens L_2;

(iii) a Moll's micro-thermopile (with a glass window and a vertical slit) mounted on the carriage of a travelling microscope capable of horizontal movement along the focal plane RV of the spectroscope, and lastly

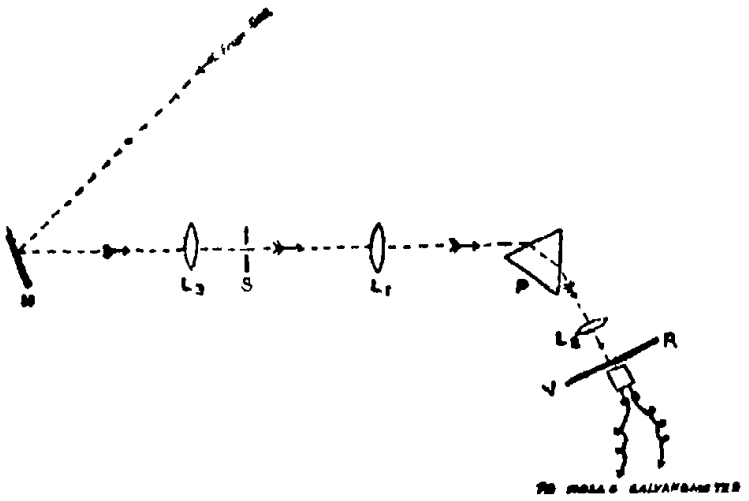


FIG 1

(iv) a sensitive Moll galvanometer (period $\frac{1}{8}$ second) (connected to the thermopile), with a lamp and scale arrangement for reading the deflections

It may be pointed out that glass is sufficiently transparent in the near infra-red region of the spectrum in which we are interested and that the whole experimental set-up has, when sunlight is focussed on the spectrograph, a maximum sensitiveness in the wavelength interval 0 75μ to 1·2μ, the deflection decreasing rapidly on either side, *i.e.*, when the thermopile is shifted towards the visible region or towards wavelengths greater than 1·2μ.

Fig. 2 is a typical curve showing the deflections in cm. on the scale against the readings of the travelling microscope in cm. The positions of the various important absorption bands are indicated in the figure It may be noticed that the chief water vapour absorption bands are

ψ' at 1 47μ

ψ at 1·42μ

ϕ at 1·13μ

ρ at 0·93μ

Fowle's absorption measurements in the laboratory with columns of moist air a few hundred metres long (using Nernst glowers as the source of radiation) were naturally confined to the intense absorption bands ϕ and ψ' In these measurements Fowle reached values of water content up to 0 5 cm. of

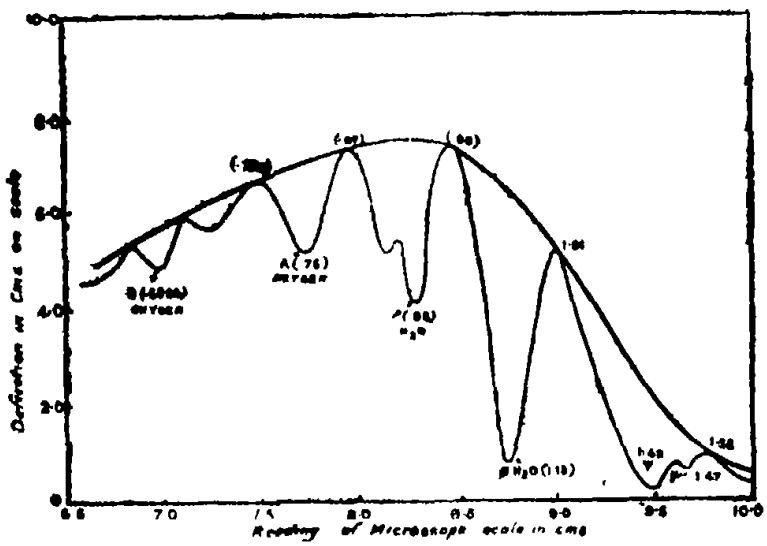


FIG 2 ABSORPTION BANDS IN THE SPECTRUM OF SUNLIGHT IN THE NEAR INFRA-RED REGION (7 TO 1 82 μ)

FIG. 2

precipitable water, W He extended the measurements to larger values of W by working at Mount Wilson with the sun as the source and with air masses up to 3 5, *i e*, at different zenith distances of the sun. Fowle's transmissibility values for the bands ϕ and ψ' have been correlated with the transmissibility values at the relatively weaker band at ρ (0 93 μ) so that the transmission of radiation at the ρ band may be used for computing the values of W. Fig. 3 gives the transmissibility at ψ' plotted against that at ρ as given by Pierre Lejay[4] and Fig 4 gives the transmissibility at ψ' against the values of W (precipitable water in cm) as given by the same author In our measurements we have recorded the transmission at ρ and used Figs 3 and 4 for computing W. The advantage in using the ρ band is that the variations in the absorption at different times or dates are larger and are recorded more accurately as the deflections in this region are comparatively larger than at the other bands The base line in Fig. 2 is obtained by screening the radiation from the instrument The transmission at ρ is obtained as the ratio of CD to O'D in Fig. 5 where OX is the base line, A and B are the maximum readings on either side of the band giving O' as

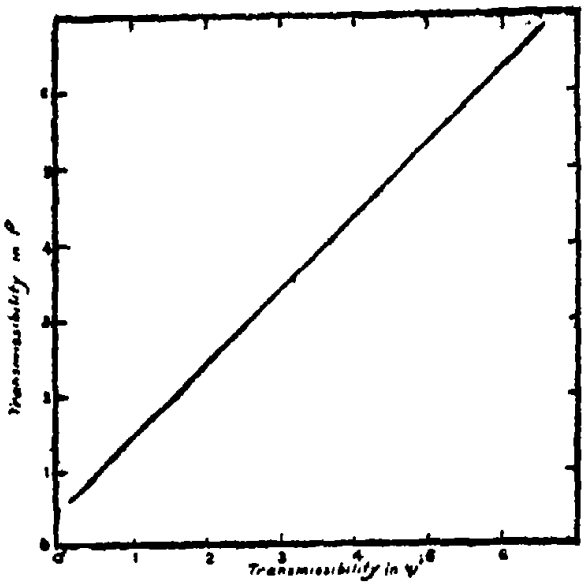


Fig 3

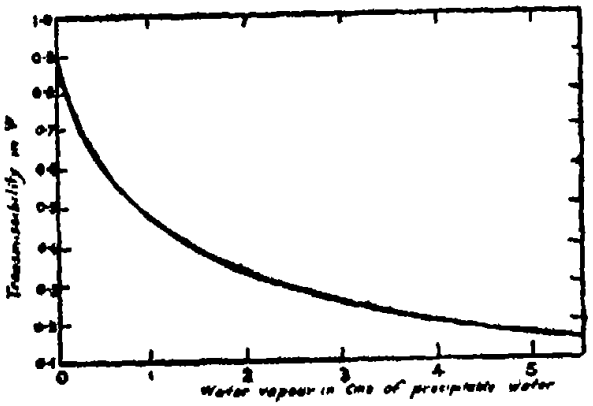


Fig 4

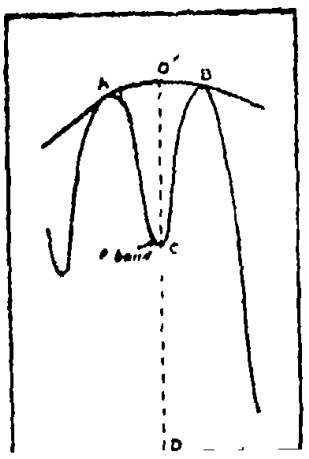


Fig 5

the point for 100% transmission and C is the minimum deflection corresponding to the centre of the absorption band ρ

3. Data Recorded and a Brief Discussion of Some of the Main Results

The observations were recorded whenever sunshine unobscured by clouds could be focussed on the spectrograph During clear weather the observations could proceed regularly at more or less fixed times, during cloudy weather one had to wait for openings in the clouds. On many or most

of the days during the wet season no observations were possible. During the period September to June the records are available for some days; the number is large during the period November to April and small in September and October and June During June to September, attempts were made to take observations during the rare occasions when the skies cleared temporarily.

Table I gives the observations recorded at different hours during the 17th February 1941 These illustrate the process of computing the values

TABLE I

Example giving observations recorded on the 17th February 1941 and the method of computing W

Hour	θ	Sec θ	D. B / W B	V P / H%	Min of ρ	Max near ρ		Max ρ	Tran in ρ	Tran in ψ'	W Sec θ	W	Whether Remarks
0820	75·5	4 000	20 2 / 15·8	11 3 / 64	0·30	2·00	2·30	2·20	·1363	·096	8·80	2·200	1 Cl
0855	67·5	2·613	21 7 / 16·5	11 5 / 59	0 52	2 00	2 30	2·20	2363	·195	4·30	1 642	1 Cl
0930	60 0	2 000	24·2 / 18 0	12 4 / 55	0 50	1 85	2·00	1 96	·2564	216	3 60	1 800	
205	34 0	1·206	31 0 / 18 8	10 2 / 30	0 85	2 25	2 30	2 29	3698	330	2 10	1 741	
235	32·5	1 186	32 2 / 18·0	8 4 / 23	0 90	2 51	2 65	2 61	3443	305	2 27	1 914	
1333	35 0	1·221	31·2 / 16 5	6 7 / 20	1 05	2 70	2 90	2 86	3671	327	2 13	1·745	
1430	42 0	1 346	33 2 / 17 5	7 1 / 19	1 00	2 50	2 70	2 63	3802	342	1 97	1 464	
600	60 0	2·000	33 5 / 18·0	7 7 / 20	0 65	2 50	2·69	2 60	2500	210	3·70	1·850	1 Cu
1653	70 5	3 000	34 0 / 18·5	8 2 / 21	0 45	2 00	2 25	2 16	2082	169	5 20	1·766	2 Cu
1730	75 5	4·000	33 0 / 18 0	8 0 / 21	0 30	1 60	1 80	1·71	1754	135	6 80	1·700	3 Cu

of W, the depth of the total precipitable water in centimetres, in a vertical column of the atmosphere 1 sq. cm. in cross-section extending up to the outer limit of the atmosphere. It will be noticed that when the sun is at a zenith distance θ, the value obtained is W sec. θ, and that W is obtained by dividing W sec. θ by the air mass sec θ at the time of observation. The dry bulb and wet bulb temperatures D.B , W B , were recorded with an Assmann Psychrometer near the instrument and the values of the vapour pressure , relative humidity are also given in the table,

(a) Seasonal and diurnal variation of W —Table II gives the mean daily values of W in cm. in different months of the period February 1941 to

TABLE II

Mean value of W in cm. in different months during different hours of the day during the period February 1941 to January 1942

(n) is the number of observations on which the means are based.

Month		0800 to 0900 hrs	0900 to 1000 hrs	1000 to 1100 hrs	1100 to 1200 hrs	1200 to 1300 hrs	1300 to 1400 hrs	1400 to 1500 hrs	1500 to 1600 hrs.	1600 to 1700 hrs
February	W	1 66	1 74	2 10	1 70	1 77	1 76	1·75	1 75	1·84
1941	(n)	(37)	(25)	(4)	(6)	(23)	(23)	(19)	(12)	(22)
March	W	1 41	1 51		1 67	1 71	1 68	1 66	1·73	1 51
1941	(n)	(45)	(27)		(5)	(25)	(19)	(22)	(10)	(24)
April	W	1 64	1 75	1 72	1 77	1 84	2 03	1 83	1 88	1·45
1941	(n)	(39)	(10)	(19)	(11)	(25)	(19)	(21)	(4)	(23)
May	W	1 73	1 63	1 99	1 87	2 15	2 34	2·02	2 14	2 39
1941	(n)	(28)	(1)	(24)	(14)	(28)	(9)	(19)	(6)	(23)
June	W	2 68	2 09	2 89	3 15	2 89	2 72	2 94	2 92	2·43
1941	(n)	(6)	(6)	(6)	(5)	(6)	(7)	(6)	(7)	(12)
July	W					.	2 72			..
1941	(n)						(3)			
August	W	.	..	.	2·53	.	.	..		..
1941	(n)				(1)					
September	W	1 87	1 72	2 07	2 36	2 30	2 03	2·48	2 76	1·65
1941	(n)	(10)	(4)	(17)	(7)	(11)	(8)	(3)	(10)	(8)
October	W	1 39	1 45	1·89	1 56	1 93	1 91	1 96	1 71	1 64
1941	(n)	(19)	(11)	(24)	(8)	(16)	(13)	(17)	(10)	(16)
November	W	1 03	1 35	1 38	1 47	1 54	1 55	1 46	1 69	1 41
1941	(n)	(13)	(14)	(20)	(9)	(18)	(13)	(11)	(14)	(22)
December*	W	0 45	0 74	0 82	1 25	1 11	1 09	0 89	1 03	0 83
1941	(n)	(3)	(3)	(8)	(5)	(8)	(9)	(6)	(5)	(8)
January*	W	0 62	0 83	1 02	1 14	1 17	1·08	1·25	1 27	1 24
1942	(n)	(4)	(8)	(9)	(12)	(19)	(9)	(9)	(17)	(15)

* *N B*—The comparatively lower values of W in the morning hours of December 1941 and January 1942 are due to the number of observations available for these hours as well as the values of W recorded on the few occasions being rather small.

January 1942 (one year) at different hours of the day The figures within brackets indicate the number of observations on which the means are based. The table based on observations so far recorded gives some idea of the diurnal variation of W in different months of the year The values are comparatively small, generally < 2 cm. during the dry season October to April. After April there is a rapid increase towards June, when the south-west monsoon sets in. All the available observations from June to August indicate values higher than 2 cm , they are higher than 2·5 cm and often 3·0 cm. or more during wet spells (*i e.*, individual occasions) Looking at the mean values of W at different hours, one finds that there is a tendency

for the values of W to increase in the afternoon and in some months like March, April, June and September a tendency later towards the evening for W to decrease On individual days the effect of sea-breeze is perceptible. A study of W in relation to the properties and sources of the air masses at different levels is being attempted.

(*b*) *Mid-day or noon values of W* —The noon values of W are recorded when the incoming solar rays are normal or nearly normal to the atmosphere, *i.e*, the air mass is nearly unity The seasonal variation of W is brought out clearly in Fig 6 where the noon values of W are plotted as dots against the dates for which the data are available during the period February 1941 to January 1942 The dots cluster about a mean value of W which is low in

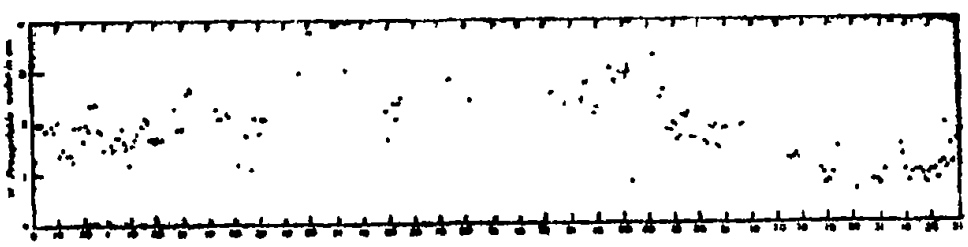


Fig 6

winter (lowest values are recorded in December) as may be seen from the two ends of the diagram The value of W increases in summer and attains a maximum value during the middle of the monsoon season (July–August). The lowest value of W so far recorded was 0 46 cm. on the 2nd December 1941 and the highest value was 3 97 cm recorded on the 4th June 1941. During the monsoon months the number of occasions when observations could be recorded was small; the seasonal tendency is, however, shown even by the few dots plotted against these months It should be pointed out that the values of W recorded during the short intervals of clear weather during the monsoon would be smaller than those during the rest of the season, so that they should be taken as the lower limit of W during the rainy season

(*c*) *Mean daily values of W in different months of the year; a comparison of these with values of W estimated by other methods.*—Columns 2, 3 and 4 in Table III give the mean daily values of W during different months of the year as computed from the spectroscopic observations during the hours falling within the zenith distance of 60° of the sun before and after noon. The available data are given separately for the years 1940, 1941 and 1942. The figures inside brackets below the values of W indicate the number of observations on which the mean values are based. It may be noticed that the values

TABLE III

Month	Mean values of W in cm. based on						
	Spectroscopic measurements made in			Normals of sounding balloon data based on 10 years' records	Measurements of heat radiation from the night sky	Hann's formula $W = 2{\cdot}1 \times e$, using	
	1940	1941	1942			Data of e recorded in 1941–42	Normal values of e computed from 50 years' records
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
January			1 16 (71)	1·52	1 46	1 08	1 76
February	1·79 (16)	1 76 (111)		2 09	2 83	1 87	1 70
March	1 61 (51)	1 69 (128)		1 88	2 85	1 64	1 86
April	1 93 (47)	1 86 (126)		3·27	3 06	1 75	2 24
May		2 17 (12)		4 23	3 05	2 42	3 02
June		2 77 (34)		4 82	2·96	3 39	3 74
July		2 72 (3)		4 80	4 36	3·56	3 79
August		2 53 (1)		5 21	4 82	3 44	3·71
September		2 31 (68)		5·11	3 94	3 44	3·64
October	1 6[illegible] (34)	1 94 (102)		3 88	3 06	2 64	3 26
November	1 5[illegible] (61)	1 46 (87)		2 67	3 07	1·77	2 36
December	0·91 (16)	1 00 (53)		2 47	1 84	1 53	1 83

of W in February, March, April, October, November and December given for both 1940 and 1941 more or less agree with each other. The seasonal variation, as already pointed out, indicates a minimum in December and a maximum during the monsoon season (June-August) In the 5th column of Table III are given the values of W computed from the normal values of e, the vapour pressure in mm. of Hg and T the temperature in degrees absolute at different levels above ground based upon 10 years' sounding balloon records. These computations were made according to the formula:

$$\delta W = \delta h/T \times \cdot 622\ e/2\ 8703 \times 10^3 \text{ cm.},$$

where δW is the precipitable water in the height interval h_1 to h_2 or δh (cm.) at mean temperature of T° A and having a vapour tension e (expressed in millibars). W is obtained by adding up the values of δW for the different

height intervals. The values of W are nearly of the same order of magnitude as the spectroscopic values only in the first three months of the year During the rest of the year the values computed from the sounding balloon records are higher This difference may partly be due to the fact that while the spectroscopic values refer only to spells of clear weather, the sounding balloon data are available for all types of weather

The values of W given in columns 7 and 8 are based on Hann's[6] formula $W = 2 \cdot 1\, e$, where e is the vapour pressure at the surface in cm of Hg The values computed from (1) the data of e during the period 1941-42 and (2) the normal values of e based on past 50 years' records are more or less similar. They are not so high as those based on the sounding balloon records but are somewhat higher than the spectroscopic values

Lastly, in column 6, we have given the estimates of W obtained from the measurements of the nocturnal heat radiation falling on unit area of a horizontal surface made with an Angstrom's Pyrgeometer at Poona during clear nights. It is well known[7,8] that the ratio of S, the heat radiation received from the night sky to the black-body radiation σT^4 emitted by the same surface at a temperature of T° A is given by

$$S/\sigma T^4 = A - B\, 10^{-kw}$$

where A, B and k are constants whose values are 0 77, 0 28 and 0·33 respectively and W is the precipitable water in the atmosphere (cm.). The values of W computed from the above formula, knowing all the factors except W, are slightly higher than the values given in columns 7 and 8, but smaller than those given in column 5. The estimates of W from the heat radiation data are not strictly comparable with the day estimates obtained spectroscopically The comparative values of W given in Table III show that the spectroscopic values are smaller than the other estimates It may be mentioned that during the month of November 1940 there were a number of days when sounding balloons had been let off at Poona and when the values of W had also been let off at Poona and when the values of W had also been determined by the spectroscopic method The values of W obtained by the two methods are given in Table IV below in the order of increasing values of W

The spectroscopic values are roughly half of the values obtained from the sounding balloon data. It is hoped that, with further improvements in these two methods of measurements, the real source of difference will be located. It is more than possible also that Fowle's original relation between W and the transmissibility of radiation at the ψ', and ϕ bands may require revision.

TABLE IV

Date	W in cm	
	Spectroscopic	Computed from sounding balloon data
18-11-1940	0 67	1 43
22-11-1940	1 40	2·42
16-11-1940	1 47	2 90
6-11-1940	1 70	4 08
14-11-1940	2 30	3 29
5-11-1940	2 38	4 26
24-11-1940	2 96	4 88

The variations in W from day to day are, however indicated unmistakably by the spectroscopic measurements which have the great advantage that the results are available immediately to the weather forecaster This aspect is dealt with in the next section.

4 W IN RELATION TO SOME WEATHER PHENOMENA

(*a*) *Effect of sea-breeze.*—On many days during the pre-monsoon months the sea-breeze with a westerly component replaces the air of land origin. On some of these occasions the marked contrast in the moisture contents of these air masses brings about an increase of W, after the sea-breeze sets in An example is given in Table V; the data refer to the 3rd of April 1941.

TABLE V

Time	W in cm	Remarks
Hrs I S T		
0905	1 97	
1045	2 16	
1130	2 29	
1305	2 25	2 Cu at 1315 hours
1406	2 15	5 Cu at 1400 hours
1640	2 39	Sea breeze started at 1655 hrs
1712	3·43	

(*b*) *Prior indications of wet weather as given by W* —The use of W in the prediction of local weather at Poona and its neighbourhood was tried out during the current year. It was found by experience that on some days during the pre-monsoon months and on a few days in September of the year 1941, an increasing tendency in W did give an indication of the following wet weather. It appears that the measurements of W, whenever possible, would be of some aid in the prediction of local weather. For example, the

first rainfall during the year 1941 occurred on the evening of the 1st April 1941, in association with a thunderstorm. The observations on this date showed a progressive increase in W. These are given in Table VI.

TABLE VI

Date	Time hrs I S T	W in cm.	Remarks
27-3-1941	Means value for each date	1 92	2 As at 1000 hrs
28-3-1941		1 99	8 Cs at 0800 hrs and 5 Cu at 1630 hrs.
29-3-1941		1 57	1 Cs at 0740 and 2 Cu at 1710 hrs
30-3-1941		1 72	4 Cu at 1400 hrs and onwards
31-3-1941		1 57	1 Cs at 0735 hrs
1-4-1941	0744	1 71	
,,	0803	1 67	
,,	0853	2·18	
,,	1232	2 21	
,,	1346	2 29	
,,	1530	2·31	6 Cu at 1510 hrs. later culminating in thunderstorm beginning at 1715 hrs and ending at 1815 hrs. 10 cents of rainfall
,,	1625	2·45	

Again, it may be remarked that the mean values of W day by day during the period 26th May to 26th June indicated the gradual onset of the monsoon on the 4th June, its weakening after the spell of rain up to the 9th June, the prevalence of a drought which persisted up to the 25th of June when the monsoon strengthened once again The data during the above period are given in Table VII.

TABLE VII

Date	Mean W in cm	Remarks
26-5-1941	2 61	
27-5-1941	2 76	
28-5-1941	2 10	
29-5-1941	2 15	
30-5-1941	2 75	
31-5-1941	2 92	7 Ci 1730 hrs onwards
1-6-1941	2 82	4 Ci 0715, 4 Cu at 1330 hrs
2-6-1941	2 92	7 Ci 1030 to 1300 hrs
3-6-1941	2 75	7 Cu and Ci at 0700, 8 Cu at 1330 and slight rain at 2000 hrs
4-6-1941	3 97	Rain at 1230 and 1430 hrs , start of monsoon
18-6-1941	1 89	
19-6-1941	1 98	
20-6-1941	1 64	6 Cu Ci at 0723 to 1230, 5 Cs at 1730 hrs
21-6-1941	3 03	
22-6-1941	2 16	Veil like cloud 1330 to 1700 hrs
23-6-1941	1 86	
24-6-1941	2 51	
25-6-1941	3 37	Thick Ci veil at 0705 hrs.
26-6-1941	3·75	Monsoon re-established with slight rain on 26th and a heavy shower on 27th.

Conclusion

The investigation is being continued. A more detailed discussion of the various aspects of the subject has been given in a thesis submitted to the Bombay University.

The author wishes to thank Dr L. A Ramdas, for suggesting the problem and for guidance during the investigation and the Director-General of Observatories for permission to work in the Meteorological Office, Poona.

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A METHOD OF ESTIMATION OF THE THICKNESS OF THE "LAMINAR" LAYER ABOVE AN EVAPORATING WATER SURFACE

By L A Ramdas and P K Raman

(From the Meteorological Office, Poona)

Received December 26, 1945

1. Introduction

When a current of air flows horizontally over a surface of water there are, as is well-known, (i) a " laminar " or " boundary " layer adjacent to the water surface, in which the air movement is stream-lined in character and (ii) a turbulent or eddying layer above the laminar layer in which there is a considerable amount of mixing The thickness of the laminary layer *decreases* rapidly with increase in the mean velocity of air current

In the laminar layer AB to CD (Fig. 1) the variation with height of factors like temperature, vapour pressure and wind velocity may be assumed to be linear ; the transfer of momentum, water vapour or heat in the laminar

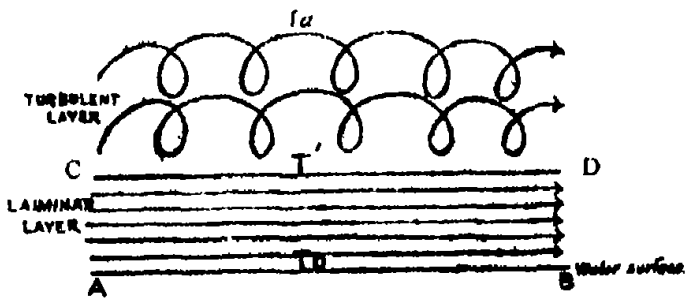


Fig 1

layer will be due to molecules, whereas in the turbulent layer the eddies take a major part in such transfer It is significant that the heat transfer between the air and the water surface will be $k \times \frac{dT}{dZ}$ where k is the molecular heat conductivity of air ($5{\cdot}77 \times 10^{-5}$) and $\frac{dT}{dZ}$ is the thermal gradient in the laminar layer With the above assumptions and from a knowledge of (*a*) the rate of evaporaton, (*b*) the vertical temperature gradient between the water surface and a series of points above the surface, and (*c*) the temperatures of the water surface and the surrounding room it is possible to estimate, under

certain favourable conditions (when the heat of evaporation is supplied entirely by the air and by radiative exchange), the thickness δ of the laminar layer and its dependence on the mean wind velocity The present paper discusses the results obtained in a preliminary investigation on the above lines

2 The Vertical Change of Temperature Inside and Above a Layer of Water

If a vessel containing water is kept exposed to the air, the variation of water temperature with depth and of the air temperature with height above the water surface will depend upon the mean temperature of the water layer, the difference of temperature between the water and the air above, the wind velocity and the rate of evaporation Fig. 2 shows the variation of temperature when measurements were made with water at different mean temperatures. The general air temperature in the room was sensibly constant during these experiments The measurements of the water temperature at various depths and of the temperature of the air just above the water surface at various heights above the surface were repeated in quick succession for various values of the mean temperature of the water layer.

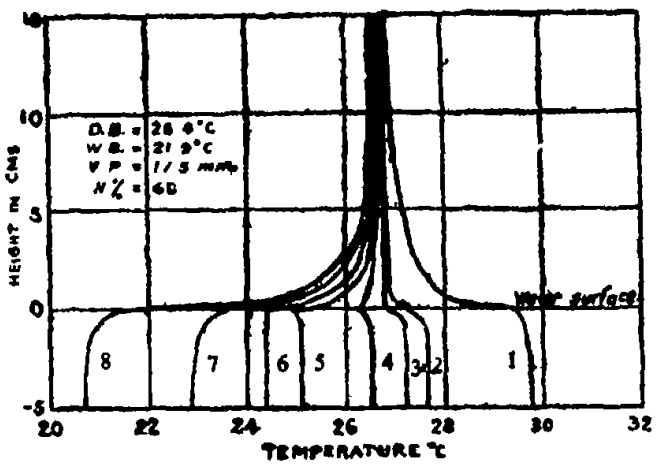


Fig 2.

A water reservoir 24 cm in diameter and 10 cm. deep was filled with water at the required tempereture The water was stirred well and then allowed to come to rest. After the water column had come to rest and the conditions above and below the water surface had become steady, the temperature measurements were made The temperatures were measured by using a series of fine copper-constantan (50 S.W G) junctions connected to a suitable switchboard and a common junction at a standard temperature.

Each junction could be connected in turn to a Moll galvanometer and the deflections recorded in quick succession. The values of temperature were read off from the calibration curve of each junction (previously determined) All the junctions were kept horizontal, except the one in contact with the water surface which was vertical with the sensitive point approaching the surface from *below* the water surface In Fig 2 the dry bulb and wet bulb temperature of the air in the room (well away from the water resorvoir) recorded with an Assmann Psychrometer together with the vapour tension and the relative humidity are also indicated Curves 1 to 8 refer to the different mean temperatures of the water column. As is to be expected, all the curves tend to meet at a sufficient height above the water surface In Curves 1 and 2 the temperature *decreases* gradually as one approaches the water surface from below The most rapid fall occurs in the first few mm *above* the water surface ; thereafter the fall of temperature is more gradual Under these conditions the water column supplies heat to the water surface for the evaporation process as well as for warming the air layers above it

Curve 3 refers to the case when the surface of the water is at the same temperature as the air above. Here there is no gradient of temperature *above* the water surface, so that the heat required for evaporation is supplied entirely by the water column In Curve 4 the mean temperatures of the air is the same as that of the water column Here there is a fall of temperature as we approach the water surface both from above as well as below, so that the heat required for evaporation is arriving by conduction both from the air as well as the water column Curve 6 is the most interesting, as the whole water column tends to remain at a uniform temperature The air temperature increases with height above the surface and the heat required for evaporation is obtained entirely by conduction from the air *above* the water surface (and by the heat gained by radiative exchange between the surface and the surroundings)

With further decrease of the mean water temperature (Curves 7 and 8) the temperature increases as one approaches the water surface from below and continues to increase with height above the water surface Here the heat conducted from the air is used partly for evaporation and partly for warming the water layer as well. When the mean temperature of the water column is at or below the dew point water vapour begins to condense on the water surface adding a further contribution of heat.

In the rest of this paper we deal only with evaporation under the simple conditions defined by Curve 6 in Fig 2 It must be remembered that no hea

is then lost by the water ; the heat required for evaporation is supplied entirely by (*a*) conduction from the air and (*b*) radiative exchange* with the surroundings. Under these simple conditions we have

where L is the latent heat of evaporation,

w is the evaporation in grammes per second,

k is the molecular thermal conductivity,

T_0 and T_a are the temperatures of the water surface and of the walls of the room (the same as the temperature of the room air),

σ is the Stefan Boltzman constant.

In the above expression, L is known, w, T_0 and T_a can be measured directly, σ is known, so that the factor $k\frac{dT}{dZ}$ can be computed This has been done for a number of wind velocities These data have been used for estimating the thickness δ of the laminar layer, as will be clear from the next section

3 Estimation of the Thickness of the Laminar Layer

The experimental arrangements are the same as in Section 2. The water reservoir is protected at the sides by a layer of heat insulating material. *In all the experiments the water layer is brought to the isothermal* condition *as defined by Curve 6 of Fig 2.* The rate of evaporation is measured by keeping a small circular dish 26·42 sq.cm in area at the centre of the water surface with a layer of water inside adjusted so as to be at the same level as that of the water surface outside. This vessel is weighed before and after each experiment, care being taken to dry the outside and keep the vessel covered during weighing The wind velocity is regulated by means of an adjustable electric fan with a wire-gauze shield in front to reduce major fluctuations After starting the fan and verifying that the water in the reservoir is isothermal, the surface temperature and the air temperature at 1, 2, 3, 5 mm. above the water surface as well as the temperature of the air in the room were measured. Table I gives the results of a series of experiments at different wind velocities. The first column gives the mean rate of evaporation during the period of half to one hour usually taken to complete each experiment. The total

* Both the water surface and the walls of the room act like "black" bodies in the

TABLE I

Evaporation in gr./cm.^{2} per sec. $\times 10^{-7}$ (w)	Wind velocity in metres per sec. (v)	H%	Isothermal temperature of water column in °C T_0	Room temperature in °C T_a	Temperature gradient in °C per cm between 0–1 mm.	0–2 mm	0–3 mm.	0–5 mm.	$Lw - \rho(T_0^4 - T_a^4) = k\frac{dT}{dZ}) \times 10^5$	$10^5 \times k_1$	k_2	k_3	k_5	$\frac{dT}{dZ}$ in laminar layer °C. per cm.	Estimated thickness of laminar layer δ	Fall of temperature ΔT°C in laminar layer $\delta \times \frac{dT}{dZ}$	Fall of temperature in laminar layer ΔT / Total fall
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
31·76	0·2	44	21 6	27 6	31 2	17·0	12·4	8·3	107 3	4 07	6·28	8 66	13 01	18·6	0·170	3 16	0 5
43·91	0·55	61	22 3	28·9	31 4	17 1	12 0	7 8	195·4	6·25	11 39	16 21	24 94	33·9	0 087	2 95	0·6
44·79	0·72	64	22·5	28 7	26 5	14 2	9 9	6·1	206·2	7 82	14 80	20 98	33 65	35 7	0 068	2·43	0·9
53·30	1 00	70	23 2	28·9	1·5	16·0	10	6 6	289 9	8 58	16 90	24 97	40 84	46 8	0 056	2·62	0 7
62·39	1·80	70	23 6	26 9	28 2	14 8	10 1	6·1	321·9	11 45	21 83	32 02	52 65	55 8	0 038	2 12	0 6

evaporation divided by the time in seconds and by the area of cross-section of the floating vessel is of the order of 30×10^{-7} to 65×10^{-7} gr./cm ^{2} sec for the range of velocities which are indicated in column (2) in metres per second The relative humidity of the air as measured with the Assmann Psychrometer is given in column (3) Column (4) gives the isothermal temperature of the water column (also temperature of water surface) The room temperature well away from the evaporimeter is given in the next column Columns (6) to (9) give the temperature gradients between 0 (surface) to 1 mm. (above surface), 0 to 2 mm. 0 to 3 mm. and 0 to 5 mm in °C. per cm Column (10) gives the values of the difference between the heat Lw used up for evaporation and the heat gained by the surface by radiative exchange with the surroundings. This difference $[Lw - \sigma(T^4_a - T^4_0)]$ is equal to the heat kdT/dZ transported to the water surface by molecular conduction across the laminar layer The evaporation and temperature measurements thus give us an estimate of the heat gained by conduction. We do not know the value of dT/dZ in the laminar layer directly, but the values of column (10) divided by the molecular heat conductivity of air ($5{\cdot}77 \times 10^{-5}$) give us estimates of this gradient; these are given in column (15).

It is well known that the gradient of temperature dT/dZ in the laminar layer will be much higher than that above it. If the mean temperature gradients between 0 to 1 mm., 0–2 mm., 0–3 mm. and 0–5 mm. are computed it will be found that as we gradually increase the distance between the water surface and the point of reference above it, the values of mean temperature gradient will *decrease*. If the figures given in column (10) are divided by

the apparent mean temperature gradients given in columns (6) to (9) we ge estimates of the apparent heat conductivities given in columns (11) to (14) In Fig. 3 these values of apparent conductivity are plotted against the distance between the surface and the point of reference used for computing the

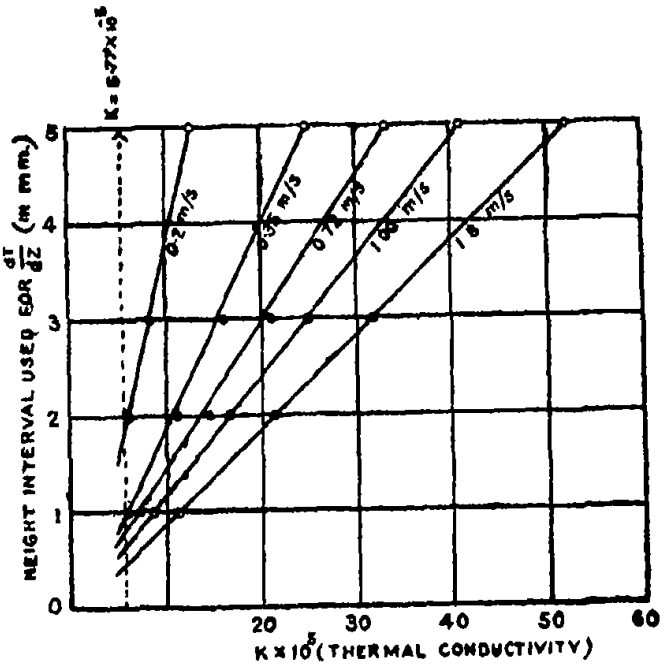


FIG 3

apparent temperature gradients The values for each wind velocity lie along a straight line, which can be produced to cut the vertical line at 5 77 × 10^{-5}, the molecular heat conductivity These points of intersection give estimates of the thickness δ of the lamina layer within which molecular heat conductivity must prevail. The values of δ are given in column (16) The values of $dT/dZ \times \delta$ representing the total fall of temperature in the laminar layer are given in column (17) In the last column the values of the ratio of the fall of temperature in the laminar layer to the total fall of temperature from the air to the water surface are given It will be seen that on an average about 6/10 of the total fall occurs in the laminar layer. The effect of increasing wind velocity is to increase the temperature gradient in the laminar layer in which about 6/10 of the temperature variation with height occurs.

Fig. 4 shows how δ, the thickness of the laminar layer, varies with the wind velocity v δ decreases with v rapidly at first and more gradually thereafter It was difficult to carry out measurements for $v > 2{\cdot}0$ metres per second,

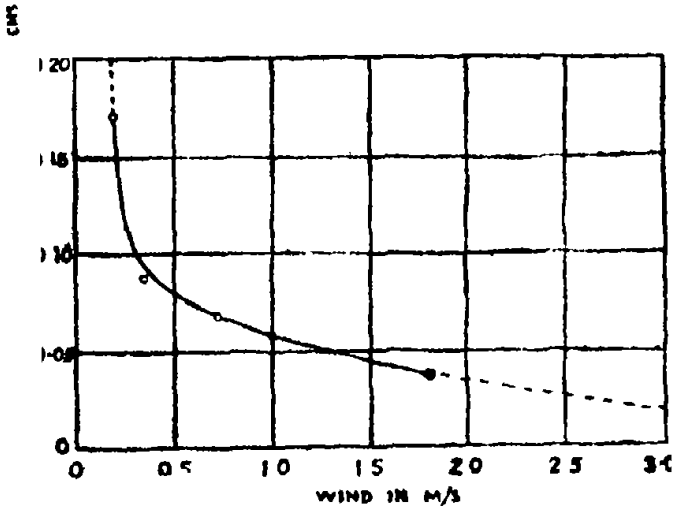


FIG 4

as the water surface began to get agitated at higher wind velocities , by extrapolation it is easy to see from Fig. 3 (dotted portion) that δ may decrease to 0·025 cm. at a wind velocity of 3 metres per second The rapid increase of δ with decrease of v towards zero is also obvious.

4 Summary and Conclusion

The present paper indicates a simple experimental method of estimating the thickness δ of the laminar layer of an evaporating water surface at different wind velocities. When the water layer is adjusted to be isothermal (*vide* Curve 6 of Fig 2) the heat Lw required for evaporation comes entirely by molecular conduction across the laminar layer $k\, dT/dZ$ and by exchange of radiation $(\sigma T_s^4 - \sigma T_a^4)$ with the surroundings From estimates of $dT/\Delta Z$ using increasing height intervals between the surface and the next level of reference, it is possible to calculate a series of k's which fall on straight lines, when plotted against the corresponding values of ΔZ. The values of ΔZ given by the points of intersection of the above lines with the vertical line at $k =$ molecular conductivity, give estimates of δ, the thickness of the laminar layer.

Further work on these lines is in progress

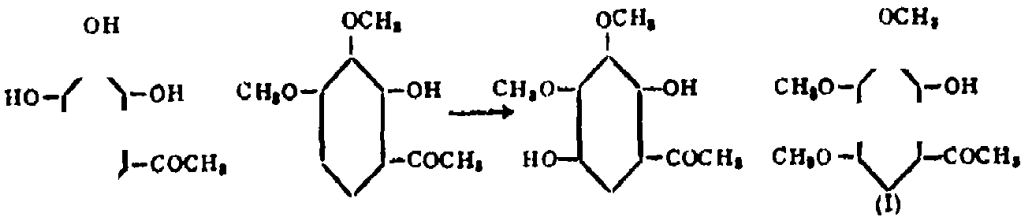
SYNTHESIS OF 6 : 7 : 8-HYDROXY-FLAVONES

By V D Nageswara Sastri and T R Seshadri

(From the Department of Chemistry, Andhra University)

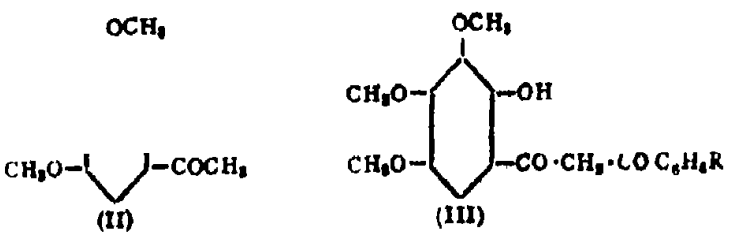
Received January 17, 1946

Flavones and flavonols derived from 1.2.3·4-tetra-hydroxy-benzene have not yet been isolated from natural sources But they form a series having three contiguous hydroxyl groups (6:7:8) in the benzo-pyrone part somewhat parallel to those derived from 1·2 3:5-tetra-hydroxy-benzene with the 5:6:7-arrangement of hydroxyls The difference in properties and reactions which this difference in structure may give rise to, is of interest and this information was required in connection with the study of plant pigments in progress in these laboratories. For purposes of comparative study the flavones of this type isomeric with baicalein and scutellarein have been synthesised and their properties described in this paper The starting material for the present synthesis is 2-hydroxy-3 4:5-trimethoxyacetophenone (I) prepared according to the method of Baker [1]

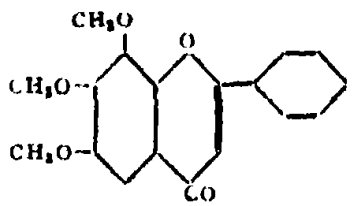


(I)

The conversion into the flavones is effected by adopting the Baker-Venkataraman procedure [2] The *O*-benzoyl or anisoyl compounds (II) are converted into the corresponding diketones (III) by means of sodamide and the final ring closure to the methoxyflavones (IV) carried out by heating with sodium acetate and acetic acid Demethylation with hydriodic acid yields the hydroxyflavones (V) They have also been characterised by the preparation of their acetates

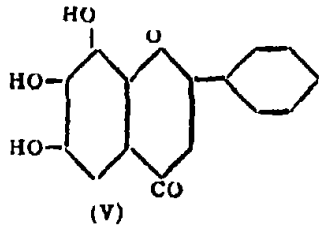


(II) (III)



(IV)

R=H, OH or OCH_3

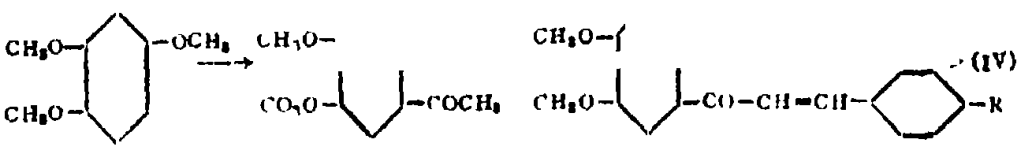


(V)

Structurally the new flavones have a hydroxyl in the 8-position in the place of the one present in the 5-position of baicalein and scutellarein Regarding fluorescence in concentrated sulphuric acid the two pairs resemble and they give very little emission. The hydroxy compounds exhibit no fluorescence; among the ethers there is feeble emission only from 6:7.8:4′-tetramethoxy-flavone In alcoholic solution neither the hydroxy compounds nor the methyl ethers give any fluorescence This is in accordance with expectations; it has been noted[3] that the 8-position in coumarins and flavylium salts is as inhibitive of fluorescence as the 5-position

The isomeric compounds differ markedly in alkali colour reactions Baicalein and scutellarein give bright green colour, the former yielding also a precipitate The 6:7:8-hydroxy-compounds are more easily soluble and give a yellow colour in sodium carbonate and orange-red in sodium hydroxide solution The ferric chloride colour is also different The 6:7:8-compounds give a deep-green colour rapidly changing to greenish blue, whereas baicalein and scutellarein give a greenish-brown, the green colour not being prominent. The reaction of the new flavones with sodium amalgam in alcoholic solution (Bargellini's test) is also somewhat different.

After the above work was completed, an abstract of a paper by Bargellini and Oliviero on the synthesis of 6:7:8-hydroxyflavones and flavonols appeared in the *British Chemical Abstracts*[4] They adopted a different method as indicated below. The melting points of the final products and their derivatives as recorded by them agree with ours



EXPERIMENTAL

2-Benzoyloxy-3 : 4 : 5-trimethoxy-acetophenone (II, R = H).—2-Hydroxy-3:4:5-trimethoxyacetophenone (I, 2·5 g.) was treated with dry pyridine

(10 c.c) and benzoyl chloride (2 c.c) and shaken well for 10 minutes. The mixture was then heated on the water-bath for 20 minutes and added to ice-water containing a few c c of dilute hydrochloric acid The benzoyl derivative separated as an oil which quickly solidified to a brown solid on stirring. It was filtered, washed with very dilute hydrochloric acid and then dissolved in sufficient quantity of ether. The ether solution was successively washed with dilute hydrochloric acid, aqueous sodium carbonate and sodium hydroxide to remove benzoic acid and unchanged ketone It was once again washed with dilute hydrochloric acid and water and dried over calcium chloride Distillation of the solvent yielded the benzoyl derivative as a colourless crystalline solid which was collected and recrystallised from alcohol and benzene It was obtained as stout irregular prisms and melted at 127–28° Yield, 2 0 g The substance gave no colour with ferric chloride in alcoholic solution and was insoluble in cold aqueous sodium hydroxide (Found C, 65 3, H, 5 3, $C_{18}H_{18}O_6$ requires C, 65 5, H, 5 5%)

2-Hydroxy-3 4 5-trimethoxydibenzoylmethane (III, R = H)—A solution of the above compound (2 g) in dry toluene (20 c c), was treated with sodamide (8 g) finely powdered under toluene. The mixture which rapidly turned yellow, was vigorously stirred for ten minutes and heated on the boiling water-bath for 4-5 hours with frequent shaking The yellow solid product was then filtered, washed well with warm benzene and cautiously added with stirring to crushed ice When the unreacted sodamide was completely decomposed, the yellow solution was filtered to remove any insoluble matter and saturated with carbon dioxide. The dibenzoylmethane separated as a bright yellow oil A further small quantity of it was obtained by extracting the toluene filtrate with 5% aqueous alkali and saturating the alkaline solution with carbon dioxide Both the lots were taken together in ether and the clear ether solution dried over sodium sulphate. The solvent was then distilled when it left an oily product which did not solidify even when allowed to stand in the refrigerator for 24 hours It was therefore directly used for conversion into the trimethoxy-flavone. Yield, 0 6 g It dissolved in aqueous sodium hydroxide to give a bright yellow solution and its solution in alcohol developed a bluish-green colouration with a drop of ferric chloride.

6.7:8-Trimethoxy-flavone (IV, R = H)—The crude dibenzoylmethane (0 5 g) was dissolved in glacial acetic acid (8 c c) and to the solution was added fused sodium acetate (2 g.) The mixture was gently boiled over a wire-gauze for 4 hours, cooled and diluted with water (80 c c). A small quantity of the trimethoxy-flavone separated as a crystalline solid. It was filtered and the filtrate extracted with ether. The ether extract was carefully shaken with 5% aqueous sodium carbonate to remove acetic acid and then

washed with water On distilling off the solvent, more of the flavone was obtained as a colourless crystalline solid The combined product was crystallised from dilute alcohol. After a further crystallisation from ethylacetate-light petroleum mixture, the trimethoxy flavone was obtained as aggregates of prismatic rods and melted at 144–45° (Bargellini and Oliviero[4] give m.p. 146°). Yield, 0·3 g. It was readily soluble in the common organic solvents and gave an orange-yellow colour with magnesium and concentrated hydrochloric acid in alcoholic solution Its solution in concentrated sulphuric acid was yellow and exhibited no fluorescence (Found. C, 69 0, H, 5 3; $C_{18}H_{16}O_5$ requires C, 69 2, H, 5 1%)

6 7 8-*Trihydroxyflavone* (*V*, $R = H$).—A solution of the trimethoxy flavone (0·25 g) in acetic anhydride (5 c c) was treated with hydriodic acid (*d*, 1 7, 5 c c) and the mixture heated at 130–35° in an oil-bath for 2 hours It was then cooled and poured into water containing sulphurous acid The precipitated yellow solid was collected, boiled with water and crystallised from alcohol. Yield, 0·15 g On recrystallisation from alcohol the trihydroxyflavone was obtained as straw-coloured rectangular micaceous plates and melted at 280–282° with slight decomposition (Bargellini and Oliviero[4] give m p 280° decomp) Its alcoholic solution developed a greenish-blue colouration on the addition of a drop of ferric chloride; with excess of the reagent a brown precipitate was deposited slowly It dissolved in concentrated sulphuric acid to an yellow solution which exhibited no fluorescence. With lead acetate in alcoholic solution it gave a bright orange-yellow precipitate, and with magnesium and hydrochloric acid its alcoholic solution developed an orange colouration When treated with sodium amalgam in absolute alcohol the trihydroxyflavone gave a green solution and a flocculent green precipitate which slowly turned brown (Bargellini's test). It dissolved in aqueous alkali to give a brownish-orange solution which gradually faded in colour; no green flocks separated. With dilute ammonia it gave an yellow solution (Found in a sample dried at 120° for 2 hours *in vacuo*: C, 66·5; H, 3 9 $C_{15}H_{10}O_5$ requires C, 66·7, H, 3 7%)

The triacetate was prepared by heating the above hydroxy-flavone (0·1 g) with acetic anhydride (5 c c) and fused sodium acetate (1 g) for two hours It was crystallised twice from ethylacetate and was obtained as stout flat needles melting at 207–08° with previous sintering at 202° (Bargellini and Oliviero[4] give m p 197–98°) (Found: C, 63 7, H, 4 3 $C_{21}H_{16}O_8$ requires C, 63·6, H, 4·1%)

2-*Anisoyloxy*-3 : 4 : 5-*trimethoxy-acetophenone* (*II*, $R = OCH_3$).—The hydroxyketone (I, 2·5 g.) was treated with dry pyridine (10 c.c.) and anisoyl

chloride (2 c.c.) and the mixture heated on the boiling water-bath for 30 minutes. The product was worked up in the same way as described for the benzoyl derivative. The crude *O*-anisoyl compound was a colourless solid which was purified by crystallisation from alcohol and then alcohol-benzene mixture. Yield, 2·0 g. A final crystallisation from alcohol yileded elongated rectangular plates and prisms melting at 114–15° It did not dissolve in cold dilute aqueous sodium hydroxide and gave no colour with ferric chloride in alcoholic solution (Found: C, 63·1; H, 5·8 $C_{18}H_{20}O_7$ requires C, 63·3; H, 5·6%)

2-*Hydroxy*-3:4.5.4'-*tetramethoxy-dibenzoylmethane* (*III*, $R = OCH_3$) — The above *O*-anisoyl derivative (2 g.) in dry toluene (20 c c.) and sodamide (8 g.) were used for the rearrangement The diketone was obtained as a heavy oil (0·7 g) which showed no tendency to solidify even when kept in the refrigerator for 24 hours and was therefore directly used for conversion into the tetramethoxyflavone. The substance dissolved in aqueous sodium hydroxide to give a deep yellow solution In alcoholic solution it gave a greenish-blue colour with ferric chloride

6:7·8.4'-*Tetramethoxyflavone* (*IV*, $R = OCH_3$) —Ring closure of the above diketone (0·5 g.) was effected by heating with glacial acetic acid (5 c.c) and fused sodium acetate (1 g) according to the procedure already described for the simpler case. The crude tetramethoxyflavone was twice crystallised from dilute alcohol when the pure compound was obtained as long colourless flat needles and melted at 179–80° (Bargellini and Oliviero[4] give m p 175–78°) Yield, 0·3 g. It was readily soluble in the common organic solvents and its alcoholic solution developed an orange-yellow colour with magnesium and hydrochloric acid It dissolved in concentrated sulphuric acid to give an yellow solution with a weak green fluorescence (Found: C, 66·9; H, 5·5; $C_{19}H_{18}O_8$ requires C, 66 7; H, 5 3%)

6:7:8:4'-*Tetrahydroxyflavone* (*V*, $R = OH$).—The demethylation of the above tetramethoxy flavone (0 2 g) was effected by boiling it for two hours with acetic anhydride (8 c.c.) and hydriodic acid (*d*, 1 7; 8 c.c.). The yellow solid obtained on dilution with water containing sulphurous acid was collected and boiled with water and recrystallised twice from alcohol. The tetrahydroxyflavone was thus obtained as aggregates of pale yellow needles and narrow rectangular plates. Yield, 0·15 g. It became orange red at 245°, dark brown at 300° and did not melt down below 330° (Bargellini and Oliviero[4] give m p. 250° with decomposition). It was moderately soluble in alcohol and acetone, and dissolved more easily in glacial acetic acid. Its alcoholic solution gave a greenish-blue colour with a drop of ferric chloride

and deposited a brown precipitate with a slight excess of the reagent. It solution in concentrated sulphuric acid was yellow and exhibited no fluorescence. When treated with sodium amalgam in absolute alcoholic solution (Bargellini's test), a greenish-brown precipitate was slowly formed. The flavone dissolved in ammonia to give an yellow solution and in aqueous sodium hydroxide to give an orange-red solution which gradually faded in colour (Found in a sample dried *in vacuo* at 120–25° for two hours: C, 62·7; H, 3·8 $C_{18}H_{10}O_8$ requires C, 62 9, H, 3 5%).

The tetraacetate was prepared by heating the above compound (0·1 g.) with acetic anhydride (5 c.c.) and fused sodium acetate (2 g.) for two hours It was crystallised twice from acetone-ethyl-acetate mixture when it was obtained as thin long needles melting at 254–55° with slight sintering at 248° (Bargellini and Oliviero[4] give m p 249°) (Found· C, 61·0, H, 4 3; $C_{26}H_{18}O_{10}$ requires C, 60 8, H, 4 0%)

Summary

6:7.8-Trihydroxy and 6:7:8.4′-tetrahydroxyflavones and their derivatives (methyl ethers and acetates) have been prepared starting with 2-hydroxy-3:4.5-trimethoxyacetophenone and adopting the Baker-Venkataraman procedure. Their properties and reactions have been studied and compared with those of the isomeric compounds, baicalein and scutellarein

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CONSTITUTION OF PATULETIN

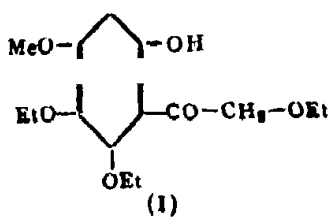
Part III. A Study and Synthesis of O-Pentaethyl Patuletin

BY L RAMACHANDRA ROW AND T. R. SESHADRI

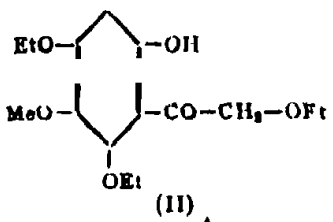
(From the Department of Chemistry, Andhra University)

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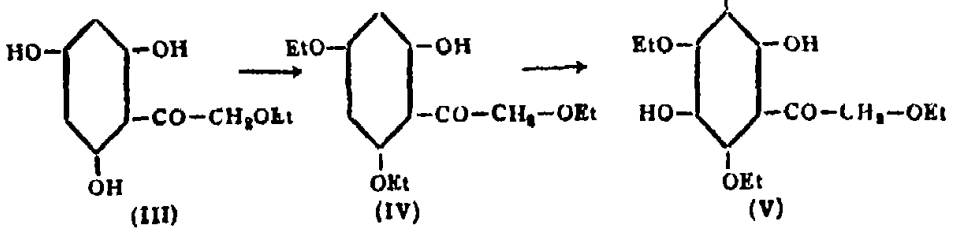
IN Part I[1] patuletin, $C_{16}H_{12}O_8$, the colouring matter of *Tagetes patula*, was shown to be a mono-methyl ether of quercetagetin. From a study of its properties and reactions and from a comparison with related compounds, the methoxyl was considered to be in the 6-position. This point has now been further investigated through the study and synthesis of pentaethyl patuletin and definite conclusions arrived at. For this purpose patuletin is fully ethylated by means of ethyl iodide and anhydrous potassium carbonate in anhydrous acetone medium The penta-ethyl ether is obtained as a colourless crystalline compound in good yield. When subjected to fission by means of alcoholic potash, it yields an acid which is identified to be *O*-diethyl protocatechuic acid both by analysis and by comparison with an authentic sample The formation of this acid as one of the products of degradation confirms the idea that the methoxyl should be situated in the benzopyrone part As the second product, an orthohydroxy acetophenone is also isolated It is not identical with quercetagetol tetraethyl ether[2] and is found to contain three ethoxyl groups and one methoxyl



(I)



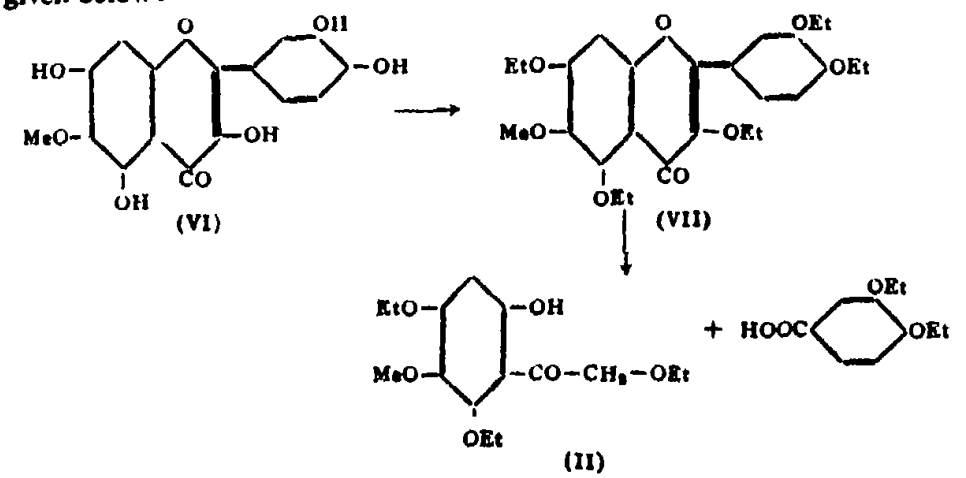
(II)



(III) (IV) (V)

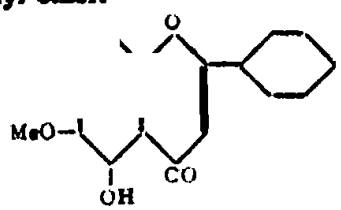
Since the properties of patuletin indicate that the 3- and 5-positions carry hydroxyl groups there are only two possible constitutions for the above

mentioned ketone: (1) ω: 5: 6-triethoxy-4-methoxy-2-hydroxy-acetophenone (I) corresponding to the 7-methoxy formula for the flavonol and (2) ω. 4: 6-triethoxy-5-methoxy-2-hydroxy acetophenone (II) corresponding to the 6-methoxy formula A ketone with the second alternative constitution has now been synthesised starting from phloroglucinol by the general methods described in Part II [3] Phloroglucinol is converted into ω-ethoxy- phloracetophenone (III) which is subjected to partial ethylation to yield ω·4 6-triethoxy-2-hydroxy-acetophenone (IV). This is found to be the same as the ketone obtained by Perkin[4] by the alkali degradation of quercetin-pentaethyl ether and called also hydroxy-fisetol-triethyl-ether The above-mentioned procedure constitutes a convenient method for its synthetic preparation Oxidation of this ketone with alkaline persulphate introduces a hydroxyl in the 5-position yielding the *p*-dihydroxy-ketone (V) whose constitution is based on well-known analogies and also supported by its properties By further partial methylation with dimethyl sulphate and potassium carbonate is obtained a product, the reactions and properties of which indicate that it has the constitution (II) This synthetic ketone is found to be identical with the degradation product from pentaethyl patuletin Further condensation of the synthetic ketone with *O*-diethyl protocatechuic anhydride and sodium *O*-diethyl protocatechuate yields a compound identical with penta-ethyl patuletin Therefore the position of the methoxyl group in the ethyl ether and consequently in patuletin is definitely fixed as the 6 and this is in agreement with all the properties and reactions of patuletin already described The above-mentioned transformations could then be represented as given below.

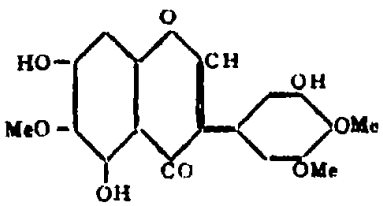


The presence of methyl ether groups in the several available positions of anthoxanthins and related anthocyanins should be of interest. In the

more fundamental 5:7-hydroxy series such as quercetin and others, the methoxyl is found commonly in the 3- and 7-positions and also in the side-phenyl nucleus. The preferential methylation of the 6-hydroxyl in patuletin is remarkable. This seems to be peculiar to the 5:6:7-arrangement of the hydroxyls. Among flavones, oroxylin-A (VIII)[5] found in *Oroxylum indicum* and 6:4'-dimethyl ether of scutellarein (IX)[6] found in the flowers of *Linaria vulgaris* could be mentioned. In the *iso*-flavone series irigenin (X)[7] is also a 6-methyl ether.



(VIII), R=H
(IX), R=OMe



(X)

Experimental

Ethylation of patuletin.—A solution of patuletin (1·0 g.) in anhydrous acetone (80 c.c.) was treated with ethyl iodide (1·5 c.c.) and anhydrous potassium carbonate (10 g.). The mixture was refluxed gently and ethyl iodide (1·5 c.c. each time; total 6 c.c.) was added at intervals of eight hours. After 30 hours, the potassium salts were separated by filtration and washed with warm acetone. The salt residue was completely soluble in water and yielded no precipitate on acidifying with dilute hydrochloric acid. The acetone filtrate was concentrated on a water-bath to about 5 c.c. and left in the ice-chest. After 24 hours, pale brown crystals separated out. The solid was filtered and washed with a small quantity of acetone. When crystallised twice from alcohol using a small quantity of animal charcoal, it came out in the form of colourless prismatic rods melting at 127–8°. Yield. 0·75 g. The pentaethyl ether was insoluble in warm aqueous alkali and gave no ferric chloride colour in alcoholic solution. It was easily soluble in acetone and ethyl acetate and moderately soluble in alcohol and benzene (Found: C, 66·6; H, 7·1; $C_{26}H_{32}O_8$ requires C, 66·1 and H, 6·8%. Total OC_2H_5 and OCH_3 expressed as OCH_3, 39·5; penta-ethoxy-monomethoxy-flavone requires 39·4%).

Alkaline degradation of O-pentaethyl-patuletin (*VII*).—*O*-Pentaethyl-petuletin (0·6 g.) was refluxed with 7% absolute alcoholic potash (20 c.c.) on a water-bath for 6 hours. The solvent was removed under vacuum and the concentrate diluted with water (75 c.c.). The solution was then acidified with hydrochloric acid and the product was extracted repeatedly with ether.

The ethereal solution was shaken thrice with dilute sodium bicarbonate solution.

The ketonic part (II).—On evaporating the ether solution a pale yellow oil was obtained which solidified on scratching with a glass-rod. When crystallised twice from aqueous alcohol, it was obtained in the form of pale yellow rhombohedral plates melting at 86–87° Yield: 0 15 g. It dissolved in sodium hydroxide giving a pale yellow solution. With ferric chloride, a reddish brown colour was obtained in alcoholic solution (Found: C, 60·6; H, 7·7, $C_{15}H_{22}O_6$ requires C, 60·4 and H, 7·4%).

Acid part.—The sodium bicarbonate extract when acidified with hydrochloric acid, yielded a white crystalline solid. It crystallised from hot water in the form of long rectangular rods melting at 165–66° and as identified to be *O*-diethyl-protocatechuic acid It did not depress the melting point of a pure sample of the diethyl ether prepared by ethylating ethyl protocatechuate with ethyl iodide and potassium carbonate in anhydrous acetone medium and hydrolysing the resulting ethyl *O*-diethyl protocatechuate with alkali (Found: C, 63·0, H, 7·0; $C_{11}H_{14}O_4$ requires C, 62 9 and H, 6·7%)

ω-Ethoxy-phloracetophenone (III).—Anhydrous phloroglucinol (7·0 g.) and ethoxy acetonitrile[8] (7·0 c.c) were condensed under the conditions of Hoesch synthesis following the method used for phloracetophenone.[9] The product crystallised from hot water in the form of stout rhombohedral prisms melting at 197–8° Yield: 7 5 g. It was easily soluble in alcohol, acetone and ether, and gave a reddish violet colour with ferric chloride in alcoholic solution (Found in a sample dried at 110–20° for three hours: C, 56 9; H, 5·8; $C_{10}H_{12}O_5$ requires C, 56·6 and H, 5·7%)

ω-4: 6-Triethoxy-2-hydroxy-acetophenone (IV).—ω-Ethoxy-phloracetophenone (2·1 g., 1 mol.) was refluxed in anhydrous acetone solution (80 c.c.) with ethyl iodide (1·8 c c, 2·2 mol) and anhydrous potassium carbonate (6 g.) for 12 hours. At the end of the reaction, the acetone was distilled of and the residue treated with water (100 c.c.) The precipitate was filtered and washed with water It was sparingly soluble in aqueous alkali. In an attempt to remove any fully ethylated ketone that might be present, the crude product was dissolved in ether and the solution extracted with 5% aqueous sodium hydroxide. The recovery was small and incomplete even after six extractions. On acidifying the alkaline solution with hydrochloric acid, a colourless crystalline solid separated out. It was crystallised twice from alcohol when ω: 4: 6-triethoxy-2-hydroxy-acetophenone (IV) was obtained in the form of thin flat needles and plates melting at 96–97°. Yield, 0·4 g.

When the remaining ether was evaporated to dryness and the residue (1 0 g.) crystallised from alcohol the same substance was obtained. The reactions and the melting points were identical and there was no depression in the mixed melting point. Thus the product of ethylation seems to consist entirely of the hydroxy-triethoxy ketone (IV) and the fully ethylated product was not present in detectable amounts.

The substance was easily soluble in alcohol, acetone and benzene. It gave a brownish red colour with ferric chloride in alcoholic solution. It was not easily soluble in aqueous sodium hydroxide and gave a sparingly soluble sodium salt (Found. C, 62·7; H, 7 8; OC_2H_5, 49 9, $C_{14}H_{20}O_6$ requires C, 62·7; H, 7·5 and OC_2H_5, 50·4%)

For purposes of comparison an authentic sample of the above ketone was prepared from quercetin (0·3 g) in the following manner. The flavonol was ethylated by boiling for 30 hours in anhydrous acetone solution with ethyl iodide (2 c c) and anhydrous potassium carbonate (2 g) The penta-ethyl ether thus obtained was subjected to fission using absolute alcoholic potash (3 c c. 7%) and refluxing for six hours After adding excess of water, it was extracted with ether From the ether solution, by shaking with aqueous sodium bicarbonate was separated *O*-diethyl-protocatechuic acid. The residual ether solution on evaporation gave a good yield of hydroxy-fisetol-triethyl ether In every respect it was identical with the synthetic sample described above and the mixed melting point was undepressed.

ω : 4 : 6-*Triethoxy*-2 · 5-dihydroxy-acetophenone (V).—To a mechanically stirred suspension of ketone (IV) (2·7 g) in water (50 c c) was added aqueous sodium hydroxide (5% 50 c c) slowly Only part of the ketone went into solution immediately and the rest dissolved completely only towards the end of the reaction The mixture was then cooled to 15° and potassium per-sulphate (4·1 g. in 100 c c of water) and aqueous sodium hydroxide (5%, 50 c c.) were added alternately during three hours while maintaining the mechanical stirring all the while. After the addition, the solution was left at room temperature for 20 hours. The insoluble portion was then filtered off and the alkaline filtrate neutralised with hydrochloric acid. The un-reacted ketone (0·8 g.) separated out and was removed by filtration The filtrate was treated with concentrated hydrochloric acid (20 c.c) and kept on a boiling water-bath for about 15 minutes. An oily layer separated out on cooling and it solidified slowly into a dark brown sticky crystalline mass. It was dissolved in ether and treated with petroleum ether till turbidity appeared On leaving it aside for about 15 minutes, a small amount of a dark brown sticky impurity separated out and the clear yellow solution could

be decanted. On evaporation it yielded yellowish brown crystals which when recrystallised from hot water came out in the form of broad square plates melting at 101–103° A second crystallisation from aqueous alcohol raised the melting point to 103–04° which could not be improved further Yield, 0·6 g With alcoholic ferric chloride it developed a transient green colour which changed rapidly to yellowish brown and finally to deep red in the course of half-an-hour. It did not give any precipitate with neutral lead acetate in alcoholic solution (Found C, 59 0, H, 6 7, $C_{14}H_{20}O_6$ requires C, 59 2 and H, 7 0%)

ω 4·6-*Triethoxy-5-methoxy-2-hydroxy-acetophenone* (II) —A solution of the dihydroxy-ketone (V) (1·0 g., 1 mol) in anhydrous benzene (60 c c) was treated with dimethyl sulphate (0·5 g, 1 1 mol) and anhydrous potassium carbonate (3 g) and the mixture refluxed for 12 hours Towards the end of the reaction, the benzene layer developed a dark brown colour The potassium salts were then filtered off and washed thrice with warm benzene The filtrate was cooled and extracted thrice with aqueous sodium hydroxide (5%, 25 c c.). When acidified with hydrochloric acid, the clear alkaline extract deposited an almost colourless crystalline solid After two crystallisations from aqueous alcohol it was obtained as colourless long rectangular plates melting at 85–86° Yield, 0 4 g It did not depress the melting point of the ketone obtained from the degradation of *O*-pentaethyl patuletin. It gave a pale reddish brown colour with ferric chroloride in alcoholic solution (Found C, 60 6; H, 7 6; $C_{15}H_{22}O_6$ requires C, 60 4 and H, 7·4%. Found total OEt and OMe calculated as methoxyl 40 9, the formula requires

O-Diethyl-protocatechuic anhydride.—Thionyl chloride (2 0 c.c) was added in small quantities at a time with vigorous shaking to a suspension of *O*-diethyl-protocatechuic acid (8 4 g) in anhydrous ether (100 c c.) containing anhydrous pyridine (10 c.c.) Throughout the addition the temperature of the reaction mixture was kept at 0° by cooling in an ice-bath After the addition was over (30–45 mts) the flask was left in the refrigerator for three hours and the mixture was shaken with crushed ice and filtered. The granular solid product was then triturated successively with ice-cold water, dilute ice-cold hydrochloric acid and ice-cold sodium carbonate solution (5%) Finally the anhydride was washed with ice-cold water until free from sodium carbonate. It was then pressed between the folds of filter paper and dried *in vacuo* over concentrated sulphuric acid. The crude product melted at 148–49° with slight sintering at 145° When recrystallised from benzene it was obtained as stout rectangular prisms melting at 149–50° Yield, 6·5 g (Found: C, 66·1; H, 6·3; $C_{12}H_{12}O_7$ requires C, 65·7 and H, 6·5%)

Synthesis of O-pentaethyl-patuletin.—An intimate mixture of ω:4:6-triethoxy-5-methoxy-2-hydroxy-acetophenone (II) (0·3 g.), O-diethyl-protocatechuic anhydride (1·0 g) and the sodium salt of O-diethyl-protocatechuic acid (0 5 g.) was heated under reduced pressure at 170–80° for four hours At the end of the reaction, the solid crust was broken up and refluxed with alcohol (10 c.c.) for about ten minutes It was then treated with alcoholic potash (1 g. of KOH in 5 c.c of alcohol) and refluxed for 15 minutes more. As much alcohol as possible was removed under reduced pressure and excess of water added to the residue. A colourless crystalline solid remained undissolved It was filtered and washed with water till free from alkali and crystallised twice from alcohol when it was obtained in the form of colourless rectangular prismatic rods melting at 128–29°. A third crystallisation was also done but it did not improve the melting point This substance did not dissolve in warm or cold aqueous alkali and developed no colour with ferric chloride in alcoholic solution Yield, 0·2 g. (Found C, 65 7; H, 6 5, $C_{26}H_{32}O_8$ requires C, 66 1 and H, 6·8%. Found total OC_2H_5 and OCH_3 calculated as OCH_3, 38 9 , pentaethoxy-mono-methoxy-flavone requires 39·4%). This product did not depress the melting point of *O*-pentaethyl-patuletin obtained by the ethylation of patuletin

The alkaline filtrate left after the separation of the above solid product was saturated with carbon dioxide. A small quantity of dark brown amorphous material was deposited Since it was too small, it was not studied.

Summary

The constitution of patuletin as 6-*O*-methyl quercetagetin has been finally established by the study of its penta-ethyl ether which yields *O*-diethyl-protocatechuic acid and ω. 4: 6-triethoxy-5-methoxy-2-hydroxy-acetophenone on degradation with alkali The above ketone and *O*-pentaethyl-patuletin have been synthesised by unambiguous methods starting from ω-ethoxy-phloroacetophenone.

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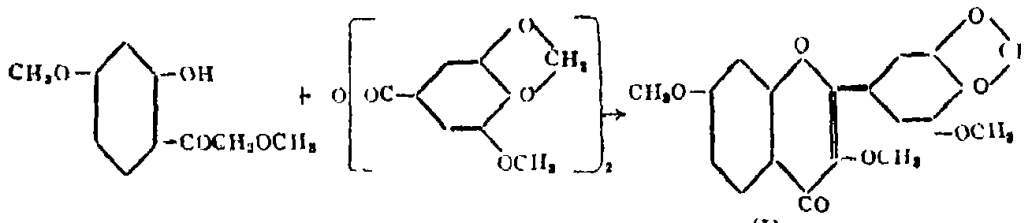
SYNTHESIS OF KANUGIN AND RELATED COMPOUNDS

By K. Visweswara Rao and T R. Seshadri

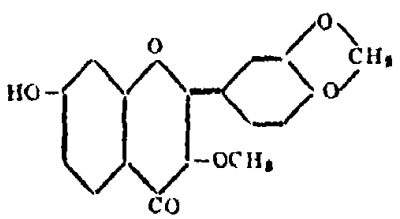
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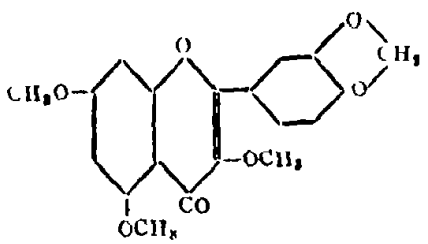
In an earlier communication[1] the determination of the constitution of kanugin (I) as 3:7.5'-trimethoxy-3'·4'-methylenedioxy-flavone was reported, based on a study of the compound and of its decomposition products This constitution has now been confirmed by synthesising kanugin from ω·4-dimethoxy-2-hydroxy-acetophenone (fisetol dimethyl ether) and the anhydride and sodium salt of myristicic acid. The synthetic product is found to be identical with the natural one in all its properties and reactions and the mixed melting point is not depressed



(I)



(II)



(III)

Since the Allan-Robinson condensation was not carried out previously with components containing methylenedioxy group and since myristicic acid is not easy to obtain, exploratory experiments have been done using first the anhydride and sodium salt of piperonylic acid The condensation with ω-methoxy-resacetophenone proceeds smoothly to yield 7-hydroxy-3-methoxy-3'.4'-methylenedioxy-flavone (II). The best yields are obtained by limiting the heating to 2-3 hours. Incidentally the condensation has also been carried out with ω.4.6-trimethoxy-2-hydroxy-acetophenone to yield 3 5:7-trimethoxy-3'·4'-methylenedioxy-flavone (III) which is designated '*iso*-kanugin'. This compound differs from kanugin in that it has

a methoxyl group in position 5 instead of in 5'. Unlike kanugin it does not exhibit fluorescence either in alcohol or in concentrated sulphuric acid. This seems to be another example of the influence of position 5, in suppressing the emission of fluorescence by anthoxanthins and related compounds.

Under the same conditions as those adopted for the preparation of the above compounds, kanugin could be obtained starting from myristicic acid. This acid was made in the past by the oxidation of isomyristicin prepared from oil of nutmeg[8] A simplified procedure has now been adopted for obtaining it in good yield from the same source. It was first made synthetically by Baker[8] from 4·5-dihydroxy-3-methoxy benzaldehyde using methylene sulphate and aqueous potash but the yields reported by him (about 5%) were very poor By a modification of the method of methylenation the yield could now be raised to 75%; 4·5-dihydroxy-3-methoxy benzaldehyde could be conveniently methylenated in anhydrous acetone solution using methylene sulphate and anhydrous potassium carbonate The product comes directly pure without any difficulty

Experimental

Piperonylic anhydride—Piperonylic acid (10 g) (dried in an air oven at 110–20° for 2–3 hours) was mixed with dry carbon tetrachloride (20 c c) and the mixture treated with powdered phosphorous pentachloride (10 g) in small amounts. It was warmed on a water-bath till no more fumes were evolved and all the solid went into solution (10 minutes). The solvent and the phosphorus oxychloride were then removed under reduced pressure on a water-bath when the acid chloride was left behind as a white crystalline solid. It was directly dissolved in anhydrous ether (100 c c) and dry pyridine (18 c.c) slowly added while cooling in ice After leaving in the ice-chest for 2½ hours, the mixture was treated with small bits of ice with vigorous stirring In about 10 minutes a pale cream-coloured solid separated out in good yield. It was filtered, washed with ice-cold dilute hydrochloric acid and ice water and dried in a vacuum desiccator Yield, 7 g. On crystallising from anhydrous benzene it came out as big colourless rectangular tablets melting at 153–4° (Found. C, 61·5; H, 2 9, $C_{16}H_{16}O_7$ requires C, 61·1; H, 3 2%). A small crystal of the compound when warmed with gallic acid and sulphuric acid formed a bright blue solution.

7-Hydroxy-3-methoxy-3'. 4'-methylenedioxy-flavone (II).—ω-Methoxy-resacetophenone (1 g) was fused with piperonylic anhydride (10 g.) and potassium piperonylate (3 g) at 170–80° for 3 hours under reduced pressure. The product was boiled with alcoholic potash (80 c.c. of 10% solution) for 20

minutes. The solvent was then removed under reduced pressure, water (100 c c.) was added and the clear brown solution saturated with carbon-dioxide when a brown solid (about 1 g.) separated out It was filtered, washed and crystallised from alcohol It came out as pale yellow rectangular plates melting at 265–67° (Found C, 65 4, H, 3 8, $C_{17}H_{12}O_6$ requires C, 65 4, H, 3 8%) The substance was soluble in aqueous alkali with a yellow colour and gave no characteristic colour with ferric chloride in alcoholic solution With gallic acid and sulphuric acid it gave a beautiful emerald green colour which rapidly changed to pure blue

3·5 7-*Trimethoxy*-3' 4'-*methylenedioxy-flavone* (*III*) (Iso-*kanugin*) — ω 4 6-Trimethoxy-2-hydroxy-acetophenone (1 g) was condensed with the anhydride (5 g) and the potassium salt (2 g) of piperonylic acid, under the conditions of the Allan-Robinson reaction After hydrolysis with alcoholic potash and removal of the solvent under reduced pressure, water was added when a pale brown solid separated out It was filtered and washed with water (Fraction A) On saturating the filtrate with carbon dioxide a yellowish brown solid separated out (Fraction B)

Fraction A (*iso*-kanugin) was crystallised from alcohol when it came out as colourless rectangular plates melting at 195–6° (Found C, 64 0, H, 4 5, $C_{19}H_{16}O_7$ requires C 64 0 H 4 5) It was insoluble in aqueous alkali and gave no colour with alcoholic ferric chloride But it gave an emerald green colour with gallic acid and sulphuric acid (test for the methylenedioxy group) Unlike kanugin it exhibited no fluorescence in alcohol and in concentrated sulphuric acid it formed a stable yellow colour It could thus be easily distinguished from kanugin

Fraction B was obtained in varying amounts in different experiments and when crystallised from alcohol it came out as a yellow crystalline solid melting indefinitely between 200 and 225° It gave a marked olive green colour with ferric chloride, was sparingly soluble in aqueous alkali and was obviously having the 5-OH free This should have arisen as the result of partial demethylation in the course of the Allan-Robinson condensation It was not further examined

Preparation of myristicic acid (1) *from oil of nutmeg* —The procedure followed for the preparation of myristicin was essentially that of Power and Salway[8] with a few modifications

Oil of nutmeg was washed with 5% alkali to remove the phenolic and acidic components It was subsequently washed with water and dried over sodium sulphate The dry oil was first distilled under reduced pressure (60 mm.) when most of the terpenes passed over below 110°. Distillation

was then effected under ordinary pressure up to a temperature of 240°. It was connected again to the pump and the distillation carried out at a pressure of 40 mm. Three fractions were collected (1) below 160°, (2) 160–70° and (3) 170–75°. The last fraction corresponded to myristicin and its yield was 10 g. from 150 c c of the oil It gave a positive test for the presence of the methylenedioxy group and the identity was further confirmed by the preparation of dibromomyristicin dibromide melting at 128–9°

The above myristicin fraction (10 g) was dissolved in alcoholic potash (alcohol 30 c c and potash 8 g) and the solution refluxed on a water-bath for 24 hours The solvent was then distilled off, the residue treated with excess of water and extracted with ether The crude isomyristicin left after evaporating the ether was directly used for the oxidation

Isomyristicin (8 g) was made into an emulsion with water (500 c.c) An aqueous solution of potassium permanganate (22 g in 500 c c) was slowly added, keeping the mixture at 80° and stirring, during the course of an hour and a half It was kept stirred for another 30 minutes by which time all the permanganate was reduced Sufficient 10 % aqueous potash was then added in order to make the mixture alkaline and the manganese dioxide formed was filtered while hot and washed with hot water From the filtrate myristicic aldehyde crystallised out on cooling This was filtered off and the solution extracted twice with ether to remove the aldehyde completely When the alkaline solution was acidified with concentrated hydrochloric acid, myristicic acid separated out It was filtered, washed with a little water and crystallised from methyl alcohol when it came out as big rectangular prisms with a tendency to taper at the ends and melting at 212–14°. Yield, 5 g

The residual manganese dioxide was suspended in water and brought into solution by passing a current of sulphur dioxide On extracting the solution with ether some more of the myristicic aldehyde could be obtained.

The total yield of the myristicic aldehyde was crystallised from water when it appeared as thin colourless rectangular plates melting at 131–32° Yield, 1 5 g The 2·4-dinitrophenylhydrazone was obtained as dark red needles melting at 230–32°

(ii) *By Synthesis* —A solution of 3-methoxy-4 5-dihydroxy benzaldehyde (2 g) and methylene sulphate (2 g.) in anhydrous acetone (30 c c.) was treated with freshly ignited potassium carbonate (10 g.) The mixture was then refluxed on a water-bath for 6 hours During the course of the reaction vigorous effervescence followed by the evolution of formaldehyde and deposition of a white solid in the cooler parts of the condenser were noticed The potassium salts were finally filtered off and the residue washed thoroughly

with acetone. The filtrate was distilled to remove the solvent when a crystalline solid was obtained. It was almost pure myristicic aldehyde and was further purified by crystallisation from water when it separated as thin colourless rectangular plates melting at 131–2° Mixed melting point with the sample of myristicic aldehyde from oil of nutmeg was not depressed Yield, 1 5 g

Myristicic anhydride —The anhydride was prepared in just the same way as piperonylic anhydride starting from the dry acid (4 g), phosphorous pentachloride (5 g.) and anhydrous pyridine (8 c c.) The crude product was obtained as a white solid, yield, 2 5 g When crystallised from anhydrous benzene it came out as stout rhombic prisms melting at 172–3° (Found C, 58 1, H, 4 1, $C_{16}H_{14}O_6$ requires C, 57 8, H, 3 7%)

3·7.5′-*Trimethoxy*-3′.4′-*methylenedioxy-flavone* (I) (*kanugin*) —An intimate mixture of ω 4-dimethoxy-2-hydroxy acetophenone (0·8 g), myristicic anhydride (2 g) and the sodium salt of myristicic acid (0 5 g) was heated under vacuum at 170 80° for 3 hours The product was cooled, powdered and boiled with alcoholic potash (30 c c of 10% solution) for 15 minutes The solvent was then distilled off under reduced pressure, the residue treated with water (100 c c) and the pale brown solid that separated out was filtered and washed It was purified by crystallisation from alcohol when it came out as colourless rectangular plates melting at 204–05° Yield, 0 8 g Mixed melting point with a pure sample of natural kanugin was not depressed (Found C, 64 4, H, 4 4, $C_{19}H_{16}O_7$ requires C, 64 0, H, 4 5)

An alcoholic solution of the compound gave a blue fluorescence In concentrated sulphuric acid it dissolved to a bright yellow solution which changed through orange to red with green fluorescence just like the natural sample With gallic acid and sulphuric acid it developed a beautiful emerald green colour.

Summary

The synthesis of 3-methoxy-7-hydroxy-3′ 4′-methylenedioxyflavone, kanugin and *iso*-kanugin has been effected Myristicic acid required for the synthesis of kanugin is prepared from oil of nutmeg by a simplified procedure and an improved method for its synthetic preparation worked out There is marked difference in properties between kanugin and *iso*-kanugin (3.5·7-trimethoxy-3′ 4′-methylene-dioxyflavone)

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A NOTE ON THE σ-SYMBOLS

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As is well known (see Van der Waerden, 1932) the symbols $\sigma^{k}_{\lambda\mu}$ are used to set up a connection between tensors and spinors for transformations of the Lorentz group k is a tensor index running from 0 to 3 while λ and μ are spinor indices which can take the values 1 and 2 only * Hitherto it has been usual to prescribe the numbers $\sigma^{k}_{\lambda\mu}$ explicitly and to show that they remain unaltered when subjected to a Lorentz transformation and the associated spinor transformation simultaneously In fact the spinor transformation associated to a given Lorentz transformation is, in effect, defined by this condition In the present paper no use will be made of an explicit representation of the σ's All their properties will be deduced from the defining equations (1) and (2) Besides compactness, this procedure has the advantage that the same equations and all their consequences remain valid even when the most general transformations not included in the Lorentz group are admitted. They can therefore be directly taken over to the general theory of relativity (*cf* Infeld and Van der Waerden, 1933)

For the present the space-time is assumed flat and the metric tensor is taken to be $g_{kl}=0$ $k\neq l$, $g_{00}=-g_{11}=-g_{22}=-g_{33}=1$ Similarly the antisymmetric spinors $\epsilon^{\lambda\mu}$, $\epsilon^{\lambda\mu}$, $\epsilon_{\lambda\mu}$, $\epsilon_{\lambda\mu}$ used for raising and lowering the spinor indices are given by $\epsilon^{12}=\epsilon_{12}=1$, $\epsilon^{12}=\epsilon_{12}=1$ For any spinor a_μ

$$a^{\lambda}=\epsilon^{\lambda\mu}a_{\mu},\quad a_{\lambda}=a^{\mu}\epsilon_{\mu\lambda}$$

with similar relations for the dotted spinors The σ's are *defined* by the two following conditions

$$\overline{\sigma^{k}_{\mu\lambda}}=\sigma^{k}_{\lambda\mu} \tag{1}$$

$$\sigma^{\lambda\mu}_{k}\,\sigma_{l\mu\dot{\nu}}=\delta^{\lambda}_{\nu}\,g_{kl}-\frac{i}{2}\epsilon\quad\sigma^{m\lambda\mu}\,\sigma^{n} \tag{2 a}$$

* In this paper Latin alphabets shall always denote tensor indices the Greek alphabets being reserved for spinor indices.

Here the bar denotes conjugate-complex and ϵ_{klmn} is a tensor antisymmetric in all the four indices with $\epsilon_{0123} = -1$. From (1) and (2*a*) it follows that

$$\sigma_{k} \; \sigma_{l, \mu\nu} = \delta^{\lambda}_{\nu} g_{kl} + i \epsilon_{klmn} \sigma^{m\lambda\mu} \sigma^{n}_{\mu\nu} \tag{2b}$$

The fact that the usual representation of σ's satisfies (2) becomes obvious when, in conformity with the usual method, one regards σ^0 as the two-rowed unit matrix and σ^1, σ^2, σ^3 as the three Pauli matrices and compares their commutation rules with (2). Some results, which are already well known (Infeld and Van der Waerden, 1933, Fierz and Pauli, 1939) follow immediately from (2)

$$\sigma^{k}_{\lambda\mu} \sigma^{l\mu\nu} + \sigma^{l}_{\lambda\mu} \sigma^{k\mu\nu} = 2\delta^{\nu}_{\lambda} g^{kl} \tag{3a}$$

$$\sigma^{k}_{\lambda\mu} \sigma^{l\mu\nu} + \sigma^{l}_{\lambda\mu} \sigma^{k\mu\nu} = 2\delta^{\nu}_{\lambda} g^{kl} \tag{3b}$$

Also

$$\sigma^{k}_{\lambda\mu} \sigma^{l\mu\nu} - \sigma^{l}_{\lambda\mu} \sigma^{k\mu\nu} = i \epsilon^{klmn} \sigma_{m\lambda\mu} \sigma^{\mu\nu}_{n}$$

$$\sigma^{k}_{\lambda\mu} \sigma^{l\mu\nu} - \sigma^{l}_{\lambda\mu} \sigma^{k\mu\nu} = i \epsilon^{kln} \sigma_{m\lambda\mu} \sigma^{\mu\nu}_{n}$$

From the irreducibility of the Pauli matrices it follows that (Fierz and Pauli, 1939)

$$\sigma^{\lambda\mu}_{k} \sigma^{k}_{\nu\rho} = 2\delta^{\lambda}_{\rho} \delta^{\mu}_{\nu} \tag{5}$$

However a direct proof based on (2) can be given as follows. Consider $\sigma^{k}_{\lambda\mu} \sigma^{l\mu\nu} \sigma^{m}_{\nu\rho}$. Notice that from (2)

$$\begin{aligned}
\epsilon_{klmn} \sigma^{k}_{\mu\lambda} \sigma^{l\lambda\rho} \sigma^{m}_{\rho\nu} &= -\frac{i}{2} \epsilon_{klmn} \epsilon^{klpq} \sigma_{p, \mu\lambda} \sigma^{\lambda\rho}_{q} \sigma^{m}_{\rho\nu} \\
&= i \left(\delta^{p}_{m} \delta^{q}_{n} - \delta^{p}_{n} \delta^{q}_{m} \right) \sigma_{p, \mu\lambda} \sigma^{\lambda\rho}_{q} \sigma^{m}_{\rho\nu} \\
&= 2i \left(g_{mn} \delta^{\rho}_{\mu} - \sigma_{n, \mu\lambda} \sigma^{\lambda\rho}_{m} \right) \sigma^{m}_{\rho\nu} \text{ from (3)} \\
&= -6i \sigma_{n, \mu\nu} \text{ from (2).}
\end{aligned} \tag{6}$$

Also from (2)

$$\sigma^{\lambda\mu}_{k}\left(\sigma_{l,\mu\nu}\,\sigma^{l}_{\alpha\beta}+\sigma_{l,\mu\beta}\,\sigma^{l}_{\alpha\nu}\right)=\delta^{\lambda}_{\nu}\,\sigma_{k,\alpha\beta}+\delta^{\lambda}_{\beta}\,\sigma_{k,\alpha\nu}$$
$$+\sum_{l}\epsilon_{klmn}\,\sigma^{m,\lambda\mu}\left(\sigma^{n}_{\mu\nu}\,\sigma^{l}_{\alpha\beta}+\sigma^{n}_{\mu\beta}\,\sigma^{l}_{\alpha\nu}\right) \quad (7)$$

Now notice that

$$\sigma^{m}_{\lambda\mu}\,\sigma^{n}_{\alpha\beta}-\sigma^{m}_{\alpha\beta}\,\sigma^{n}_{\lambda\mu}=\epsilon_{\lambda\alpha}\,\sigma^{m}_{\gamma\mu}\,\sigma^{n,\gamma}_{\beta}+\epsilon_{\mu\beta}\,\sigma^{m}_{\alpha\rho}\,\sigma^{n}_{\lambda}{}^{\rho} \quad (8)$$

Therefore

$$\epsilon_{klmn}\,\sigma^{m\lambda\mu}\left(\sigma^{n}_{\mu\nu}\,\sigma^{l}_{\alpha\beta}+\sigma^{n}_{\mu\beta}\,\sigma^{l}_{\alpha\nu}\right)$$
$$=\tfrac{1}{4}\,\epsilon_{klmn}\,\sigma^{m,\lambda}_{\alpha}\left(\sigma^{n}_{\nu\mu}\,\sigma^{l,\mu}_{\beta}+\sigma^{n}_{\beta\mu}\,\sigma^{l,\mu}{}_{\nu}\right)$$
$$=\tfrac{1}{4}\,\epsilon_{klmn}\left[\left(\delta^{\lambda}_{\nu}\,\sigma^{m}_{\alpha\rho}\,\sigma^{n,\rho\mu}\,\sigma^{l}_{\mu\beta}-\sigma^{m}_{\nu\gamma}\,\sigma^{n,\lambda\gamma}\,\sigma^{l}_{\alpha\beta}\right)\right.$$
$$\left.+\left(\delta^{\lambda}_{\beta}\,\sigma^{m}_{\alpha\rho}\,\sigma^{n,\rho\mu}\,\sigma^{l}_{\mu\nu}-\sigma^{m}_{\beta\gamma}\,\sigma^{n,\lambda\gamma}\,\sigma^{l}_{\alpha\nu}\right)\right]$$
$$=\tfrac{1}{2}\,l\left(\delta^{\lambda}_{\nu}\,\sigma_{k,\alpha\beta}+\delta^{\lambda}_{\beta}\,\sigma_{k,\alpha\nu}\right)+\tfrac{1}{4}\,\epsilon_{klmn}\,\sigma^{m,\lambda\mu}\left(\sigma^{n}_{\mu\nu}\,\sigma^{l}_{\alpha\beta}+\sigma^{n}_{\mu\beta}\,\sigma^{l}_{\alpha\nu}\right)$$
from (6)

Therefore

$$\epsilon_{klmn}\,\sigma^{\lambda\mu}\left(\sigma^{n}_{\mu\nu}\,\sigma^{l}_{\alpha\beta}+\sigma^{n}_{\mu\beta}\,\sigma^{l}_{\alpha\nu}\right)=2l\left(\delta^{\lambda}_{\nu}\,\sigma_{k,\alpha\beta}+\delta^{\lambda}_{\beta}\,\sigma_{k,\alpha\nu}\right) \quad (9)$$

From (7) and (9) it follows that

$$\sigma^{\lambda\mu}_{k}\left(\sigma_{l,\mu\nu}\,\sigma^{l}_{\alpha\beta}+\sigma_{l,\mu\beta}\,\sigma^{l}_{\alpha\nu}\right)=0.$$

Multiplying by $\sigma^{\kappa}_{\rho\lambda}$ and using (2) one gets

$$\sigma_{l,\mu\nu}\,\sigma^{l}_{\alpha\beta}+\sigma_{l,\mu\beta}\,\sigma^{l}_{\alpha\nu}=0 \quad (10\,a)$$

Now

$$\sigma_{l,\mu\nu}\,\sigma^{l}_{\alpha\beta}-\sigma_{l,\mu\beta}\,\sigma^{l}_{\alpha\nu}=\epsilon_{\nu\beta}\,\sigma_{l,\mu\rho}\,\sigma^{l\rho}_{\alpha}$$
$$=4\epsilon_{\nu\beta}\,\epsilon_{\mu\alpha} \text{ from (2)} \quad (10\,b)$$

(5) follows immediately from (10).

A few other useful relations can be derived from (2) Put

$$\sigma^{k}_{\mu\lambda}\,\sigma^{l,\lambda\rho}\,\sigma^{m}_{\rho\nu}=\mathrm{A}^{klm}_{\mu\nu}$$

Then from (3)

$$\begin{aligned}
A^{klm}_{\mu\nu} &= A^{klm}_{\mu\nu} \\
&= -A^{lkm}_{\mu\nu} + 2g^{kl}\,\sigma^{m}_{\mu\nu} \\
&= A^{lmk}_{\mu\nu} + 2g^{kl}\,\sigma^{m}_{\mu\nu} - 2g^{km}\,\sigma^{l}_{\mu\nu} \\
&= -A^{mlk}_{\mu\nu} + 2g^{kl}\,\sigma^{m}_{\mu\nu} - 2g^{km}\,\sigma^{l}_{\mu\nu} + 2g^{lm}\,\sigma^{k}_{\mu\nu} \\
&= A^{mkl}_{\mu\nu} - 2g^{km}\,\sigma^{l}_{\mu\nu} + 2g^{lm}\,\sigma^{k}_{\mu\nu} \\
&= -A^{kml}_{\mu\nu} + 2g^{lm}\,\sigma^{k}_{\mu\nu}
\end{aligned}$$

Adding up the various expressions on the right one gets

$$6\,A^{klm}_{\mu\nu} = -\epsilon^{klmn}\,\epsilon_{npqr}\,A^{pqr}_{\mu\nu} + 6\,(g^{kl}\,\sigma^{m}_{\mu\nu} - g^{km}\,\sigma^{l}_{\mu\nu} + g^{lm}\,\sigma^{k}_{\mu\nu})$$

so that from (6)

$$\sigma^{k}_{\mu\lambda}\,\sigma^{l,\,\lambda\rho}\,\sigma^{m}_{\rho\nu} = g^{kl}\,\sigma^{m}_{\mu\nu} - g^{km}\,\sigma^{l}_{\mu\nu} + g^{lm}\,\sigma^{k}_{\mu\nu} + i\epsilon^{klmn}\,\sigma_{n,\,\mu\nu} \qquad (11\,a)$$

The conjugate-complex equation is

$$\sigma^{k}_{\mu\lambda}\,\sigma^{l\,\lambda\rho}\,\sigma^{m}_{\rho\nu} = g^{kl}\,\sigma^{m}_{\mu\nu} - g^{km}\,\sigma^{l}_{\mu\nu} + g^{lm}\,\sigma^{k}_{\mu\nu} - i\epsilon^{klmn}\,\sigma_{n\,\mu\nu} \qquad (11\,b)$$

From (3 *c*) and (11)

$$\sigma^{k}_{\mu\lambda}\,\sigma^{l,\,\lambda\rho}\,\sigma^{m}_{\rho\nu}\,\sigma^{n,\,\nu\mu} = 2\,(g^{kl}\,g^{mn} - g^{km}\,g^{ln} + g^{kn}\,g^{lm} + i\epsilon^{klmn}) \qquad (12\,a)$$

$$\sigma^{k}_{\mu\lambda}\,\sigma^{l,\lambda\rho}\,\sigma^{m}_{\rho\nu}\,\sigma^{n,\,\nu\mu} = 2\,(g^{kl}\,g^{mn} - g^{km}\,g^{ln} + g^{kn}\,g^{lm} - i\,\epsilon^{klmn}) \qquad (12\,b)$$

From (4) and (12) the following well-known relations for any anti-symmetric tensor F_{kl} (Laporte and Uhlenbeck, 1931, Fierz and Pauli, 1939) are obtained immediately

$$F_{mn} = \tfrac{1}{4}\,\sigma^{\alpha\lambda}\,\sigma^{\beta\mu}_{mn}\,(\epsilon_{\alpha\beta}\,f_{\lambda\mu} + \epsilon_{\lambda\mu}\,f_{\alpha\beta}) \qquad (13\,a)$$

$$f^{\rho}_{\mu}\,\sigma^{m,\,\mu\nu}\,\sigma^{n}_{\nu\rho} = 4\,F^{+mn} \qquad (13\,b)$$

$$f^{\rho}_{\mu}\,\sigma^{mn\mu\nu}\,\sigma^{n}_{\nu\rho} = 4\,F^{-mn} \qquad (13\,c)$$

where

$$f^{\rho}_{\mu} = \tfrac{1}{2} F_{kl} \sigma^{k}_{\mu\lambda} \sigma^{l,\lambda\rho} = \tfrac{1}{2} F^{+}_{kl} \sigma^{k}_{\mu\lambda} \sigma^{l,\lambda\rho} \tag{14 a}$$

$$f^{\rho}_{\dot{\mu}} = \tfrac{1}{2} F_{kl} \sigma^{k}_{\alpha\lambda} \sigma^{l,\lambda\rho} = \tfrac{1}{2} F^{-}_{kl} \sigma^{k}_{\mu\lambda} \sigma^{l,\lambda\rho} \tag{14 b}$$

and

$$F^{+}_{kl} = \tfrac{1}{2}(F_{kl} - i F^{*}_{kl})$$

$$F^{-}_{kl} = \tfrac{1}{2}(F_{kl} + i F_{kl})$$

$$F_{kl} = \tfrac{1}{2} \epsilon_{klmn} F^{mn}$$

It is yet to be proved from (2) that for every proper Lorentz transformation there exists a spinor transformation such that the two applied together leave $\sigma^{k}_{\lambda\mu}$ unchanged For this purpose it is sufficient to consider infinitesimal transformations An infinitesimal Lorentz transformation is given by

$$x'_{k} = x_{k} + \epsilon^{l}_{k} x_{l} \quad (\epsilon_{kl} = -\epsilon_{lk}) \tag{15}$$

where ϵ_{kl} is a real infinitesimal quantity. Similarly an infinitesimal spinor transformation

$$a'_{\mu} = a_{\mu} + \eta^{\nu}_{\mu} a_{\nu} \quad (\eta_{\mu\nu} = \eta_{\mu\nu}) \tag{16 a}$$

$$a'_{\mu} = a_{\mu} + \eta^{\nu}_{\mu} a_{\nu} \quad (\eta_{\mu\nu} = \eta_{\mu\nu}) \tag{16 b}$$

is characterised by an infinitesimal spinor $\eta_{\mu\nu}$ The symmetry of $\eta_{\mu\nu}$ in μ, ν follows from the invariance of $\epsilon_{\mu\nu}$ It is therefore sufficient to show that for every ϵ^{kl} there exists a $\eta_{\mu\nu}$ such that

$$\epsilon^{kl} \sigma_{l,\alpha\lambda} + \eta^{\beta}_{\alpha} \sigma_{\beta\lambda} + \eta^{\mu}_{\lambda} \sigma^{k}_{\alpha\mu} = 0 \tag{17}$$

From (5) and (17) the solution is easily obtained

$$\eta_{\alpha\beta} = \tfrac{1}{4} \epsilon^{kl} \sigma_{k,\alpha\lambda} \sigma^{\lambda}_{l,\beta} \quad \eta_{\alpha\beta} = \eta_{\alpha\beta} = \tfrac{1}{4} \epsilon^{kl} \sigma_{k,\alpha\lambda} \sigma^{\lambda}_{l,\beta} \tag{18}$$

The transformation matrix of (16) is therefore

$$\delta^{\beta}_{\alpha} + \tfrac{1}{4} \epsilon^{kl} \sigma_{k,\alpha\lambda} \sigma^{\lambda\beta}_{l} \tag{19a}$$

$$\delta^{\beta}_{\dot{\alpha}} + \tfrac{1}{4} \epsilon^{kl} \sigma_{k,\alpha\lambda} \sigma^{\lambda\beta}_{l} \tag{19b}$$

It must now be shown that the transformation (19) considered as a representation of the Lorentz group satisfies the integrability conditions (see Van der Waerden, 1932) In any representation of the Lorentz group the transformation (15) is represented by

$$1+\tfrac{1}{2}\epsilon^{kl}\,\mathrm{I}_{kl}$$

where $\mathrm{I}^{kl}=-\mathrm{I}^{lk}$ are the representative matrices for the infinitesimal transformations (see Van der Waerden *l c*). Therefore in our case, from (19)

$$(\mathrm{I}_{kl})^{\beta}_{\alpha}=\tfrac{1}{4}(\sigma_{k,\,\alpha\lambda}\,\sigma_{l}^{\lambda\beta}-\sigma_{l,\,\alpha\lambda}\,\sigma_{k}^{\lambda\beta}) \tag{20}$$

where α and β on the left side are to be looked upon as matrix indices The integrability conditions for the Lorentz group are well known and are

$$\mathrm{I}^{kl}\,\mathrm{I}^{mn}\quad\mathrm{I}^{mn}\,\mathrm{I}^{kl}=\quad g^{km}\,\mathrm{I}^{ln}+g^{lm}\,\mathrm{I}^{kn}+g^{kn}\,\mathrm{I}^{lm}-g^{ln}\,\mathrm{I}^{km} \tag{21}$$

Now from (4) and (20)

$$(\mathrm{I}_{kl})^{\beta}_{\alpha}=-\frac{1}{2}\,\epsilon_{klmn}\,(\mathrm{I}^{mn})^{\beta}_{\alpha}=-\frac{1}{4}\,\epsilon_{klmn}\,\sigma^{m}_{\alpha\lambda}\,\sigma^{n,\lambda\beta}$$

Therefore

$$(\mathrm{I}_{kl}\,\mathrm{I}_{mn}-\mathrm{I}_{mn}\,\mathrm{I}_{kl})^{\gamma}_{\alpha}=-\frac{1}{16}\,(\epsilon_{klpq}\,\epsilon_{mnrs}-\epsilon_{mnpq}\,\epsilon_{klrs})\,\sigma^{p}_{\alpha\lambda}\,\sigma^{q\lambda\rho}\,\sigma^{r}_{\beta\mu}\,\sigma^{s,\mu\gamma}$$

$$=-\frac{1}{16}\,\epsilon_{klpq}\,\epsilon_{mnrs}\,\{\sigma^{k}_{\alpha\lambda}\,\sigma^{q,\,\lambda\beta}\,\sigma^{r}_{\beta\mu}\,\sigma^{s,\,\mu\gamma}-\sigma^{l}_{\alpha\lambda}\,\sigma^{r,\,\lambda\beta}\,\sigma^{q}_{\beta\mu}\,\sigma^{p,\,\mu\gamma}\}$$

$$=-\frac{1}{16}\,\epsilon_{klpq}\,\epsilon_{mnrs}\,\{-2g^{pr}\,\sigma^{q}_{\alpha\mu}\,\sigma^{s,\,\mu\gamma}+i\,\epsilon^{pqrt}\,\sigma_{t,\,\alpha\mu}\,\sigma^{s,\,\mu\gamma}$$

$$+2\,\sigma^{s}_{\alpha\lambda}\,g^{rp}\,\sigma^{q,\,\lambda\gamma}+i\,\sigma^{s}_{\alpha\lambda}\,\epsilon^{rqpt}\,\sigma_{t}^{\lambda\gamma}\}\ \text{from (11)}$$

$$=-\frac{1}{16}\,\epsilon_{klpq}\,\epsilon_{mnrs}\,\{-8\,g^{pr}\,(\mathrm{I}^{qs})^{\gamma}_{\alpha}+4\,i\,\epsilon^{pqrt}\,(\mathrm{I}^{s}_{t})^{\gamma}_{\alpha}\}$$

Therefore

$$\mathrm{I}_{kl}\,\mathrm{I}_{mn}-\mathrm{I}_{mn}\,\mathrm{I}_{kl}=\tfrac{1}{2}\,\epsilon^{r}_{klq}\,\epsilon_{mnrs}\,\mathrm{I}^{qs}-\frac{i}{4}\,\epsilon_{klpq}\,\epsilon_{mnrs}\,\epsilon^{pqrt}\,\mathrm{I}^{s}_{t}$$

$$=-\tfrac{1}{2}\,(\sum_{klq}\pm g_{klx}\,g_{lm}\,g_{qs})\,\mathrm{I}^{qs}+\frac{i}{2}\,\epsilon_{mnrs}\,(\delta^{r}_{k}\,\delta^{s}_{l}-\delta^{s}_{l}\,\delta^{t}_{k})\,\mathrm{I}^{l}_{s}$$

Where the sum is to be taken over all permutations of k, l, q with $+$ or $-$ sign according as the permutation is even or odd. So

$$\mathrm{I}_{kl}\,\mathrm{I}_{mn}-\mathrm{I}_{mn}\,\mathrm{I}_{kl}=-\tfrac{1}{2}\,(\sum_{klq}\pm g_{km}\,g_{ln}\,g_{qs})\,\mathrm{I}^{qs}+\frac{i}{2}\,(\epsilon_{mnks}\,\mathrm{I}^{s}_{l}-\epsilon_{mnls}\,\mathrm{I}^{s}_{k})$$

$$=\tfrac{1}{2}\,[-g_{km}\,\mathrm{I}_{ln}+g_{lm}\,\mathrm{I}_{kn}+g_{kn}\,\mathrm{I}_{lm}-g_{ln}\,\mathrm{I}_{km}]$$

$$+\tfrac{1}{2}\,(\epsilon_{mnks}\,\epsilon^{s}_{lpq}\,\mathrm{I}^{pq}-\epsilon_{mnls}\,\epsilon^{s}_{kpq}\,\mathrm{I}^{pq})$$

$$=[-g_{km}\,\mathrm{I}_{ln}+g_{lm}\,\mathrm{I}_{kn}+g_{kn}\,\mathrm{I}_{lm}-g_{ln}\,\mathrm{I}_{km}]$$

Therefore (21) is fulfilled.

It is now possible to consider finite Lorentz transformations. Let the transformations (15) be denoted by $1+\frac{1}{2}\epsilon_{kl}J^{kl}$. The transformation matrix of (15) is

$$\delta^i_k + \epsilon^i_k$$

Therefore

$$\tfrac{1}{2}(\epsilon_{kl}J^{kl})^n_m = \epsilon^n_m \tag{22}$$

where m and n are the matrix indices of the transformation J^{kl}. A finite Lorentz transformation L can be generated from the infinitesimal transformation by the following common device.

$$L = \left(1+\tfrac{1}{2}\frac{\theta^{kl}}{n}J_{kl}\right)^n_{\lim n\to\infty} = e^{\frac{1}{2}\theta^{kl}J_{kl}}$$
$$= 1+\tfrac{1}{2}\theta^{kl}J_{kl}+\frac{(\frac{1}{2}\theta^{kl}J_{kl})^2}{2!}+\frac{(\frac{1}{2}\theta^{kl}J_{kl})^3}{3!}+$$

On account of (22) one can write symbolically

$$L = e^{\theta} = 1+\theta+\frac{\theta^2}{2!}+\frac{\theta^3}{3!}+$$

where θ^n is a matrix defined by induction as follows

$$(\theta^{n+1})_p{}^q = (\theta^n)_p{}^r\,\theta_r{}^q$$

It is easy to verify that

$$\theta_{kl}\,\theta^{lm}\,\theta_{mn}\,\theta^{np}+\tfrac{1}{2}(\theta_{mn}\,\theta^{mn})\,\theta_{kl}\,\theta^{lp}-(\tfrac{1}{8}\theta^{lm}\,\theta^{nr}\,\epsilon_{lmnr})^2\,\delta^p_k = 0$$

for any tensor θ_{kl} whose only non-vanishing components are $\theta_{03}=-\theta_{30}$ and $\theta_{12}=-\theta_{21}$. However since every antisymmetrical tensor can be brought to this form by a Lorentz transformation it follows that the above identity is valid for every θ_{kl}. Written in matrix form it becomes

$$\theta^4+\tfrac{1}{2}\theta_{kl}\,\theta^{kl}\,\theta^2-(\tfrac{1}{8}\theta^{kl}\,\theta^{mn}\,\epsilon_{klmn})^2 = 0$$

Making use of this characteristic equation of θ, it can be proved that

$$L = \tfrac{1}{2}[\cosh\sqrt{\Phi_+}+\cosh\sqrt{\Phi_-}]+\frac{\cosh\sqrt{\Phi_+}-\cosh\sqrt{\Phi_-}}{\Phi_+-\Phi_-}(\theta^2+\tfrac{1}{4}\theta_{kl}\,\theta^{kl})$$
$$+\tfrac{1}{2}\left[\frac{\sinh\sqrt{\Phi_+}}{\sqrt{\Phi_+}}+\frac{\sinh\sqrt{\Phi_-}}{\sqrt{\Phi_-}}\right]\theta$$
$$+\left(\frac{\sinh\sqrt{\Phi_+}}{\sqrt{\Phi_+}}-\frac{\sinh\sqrt{\Phi_-}}{\sqrt{\Phi_-}}\right)\frac{1}{\Phi_+-\Phi_-}(\theta^3+\tfrac{1}{4}\theta_{kl}\,\theta^{kl}\,\theta) \tag{23 a}$$

where

$$\Phi_\pm = -\tfrac{1}{4}\theta_{kl}\,\theta^{kl}\pm\tfrac{1}{4}\sqrt{(\tfrac{1}{2}\theta^{kl}\,\theta^{mn}\,\epsilon_{klmn})^2+(\theta^{kl}\,\theta_{kl})^2} \tag{23 b}$$

This is the expression for the most general proper Lorentz transformation.

The spinor transformation A associated to (23) is given by

$$A = \left(1+\tfrac{1}{2}\frac{\theta^{kl}I_{kl}}{n}\right)^n_{\lim n\to\infty} = e^{\frac{1}{2}\theta^{kl}I_{kl}}$$
$$= 1+(\tfrac{1}{2}\theta^{kl}I_{kl})+\frac{(\frac{1}{2}\theta^{kl}I_{kl})^2}{2!}+\cdots\cdots \tag{24}$$

Now

$$[(\tfrac{1}{2}\theta^{kl}\,\mathrm{I}_{kl})^2]^{\gamma}_{\alpha} = (\tfrac{1}{2}\theta^{kl}\,\mathrm{I}_{kl})^{\beta}_{\alpha}\,(\tfrac{1}{2}\theta^{mn}\,\mathrm{I}_{mn})^{\gamma}_{\beta}$$

$$= \frac{1}{16}\,\theta^{kl}\,\theta^{mn}\,\sigma_{k,\,\alpha\lambda}\,\sigma_{l}^{\lambda\beta}\,\sigma_{m,\,\beta\mu}\,\sigma_{n}^{\mu\gamma}$$

$$= \frac{1}{16}\,\theta_{kl}\,\theta_{mn}\,(-2g^{km}\,\sigma_{\alpha\mu}^{l}\,\sigma^{n,\,\mu\gamma} + i\,\epsilon^{klmp}\,\sigma_{p,\,\alpha\mu}\,\sigma^{n,\,\mu\gamma}) \text{ from (11)}$$

$$= -\tfrac{1}{8}\,\theta_{kl}\,\theta^{kl}\,\delta_{\alpha}^{\gamma} + \frac{i}{16}\,\theta_{kl}\,\theta_{mn}\,\epsilon^{klmp}\,\{\delta_{p}^{n}\,\delta_{\alpha}^{\gamma} - i\,\epsilon_{prs}^{\;\;\;

In the usual representation σ^0 is the unit matrix and $\sigma^{3\cdot\alpha\beta} = -\sigma^3_{\alpha\beta}$ Therefore in matrix notation (27*a*) and (27*b*) can be written as

$$A = \cos\phi - i\sin\phi\ \sigma^3$$

$$A = \cosh\phi - \sinh\phi\sigma^3$$

where the matrix elements of σ^3 are $\sigma^0_{\alpha\beta}$

Till now only the proper Lorentz transformations have been discussed. Reflection can now be included in the following way. From (11)

$$\sigma^{0,\lambda}_{\mu}\ \sigma^{k}_{\lambda\rho}\ \sigma^{0,\rho}_{\nu} = 2g^{0k}\ \sigma^{0}_{\mu\nu} - \sigma^{\lambda}_{\mu\nu} - g^{lk}\ \sigma^{l}_{\mu\nu} \tag{28}$$

Therefore $\sigma^{0\lambda}_{\mu}$ is the reflection matrix, and by reflection the spinors a_μ and b_μ go over into a_μ and b_μ given by

$$a_\mu = \sigma^{0,\lambda}_{\mu}\ a_\lambda, \quad b_\mu = \sigma^{0\ \lambda}_{\mu}\ b_\lambda \tag{29}$$

The quantities $\sigma^k_{\mu\nu}$ remain unchanged for the simultaneous application of reflection to the tensor index k as well as to the spinor indices μ, ν In the usual representation $\sigma^0_{\mu\nu}$ is the unit matrix and therefore the only non-vanishing components of $\sigma^{0\lambda}_{\mu}$ are $\sigma^{0,2}_1 = -\sigma^{0\ 1}_2 = -1$ In this case therefore (29) coincides with the usual rules for reflection

If $\sigma^k_{\lambda\mu}$ and $\sigma'^k_{\lambda\mu}$ be two different sets of σ's satisfying (1) and (2) then it follows from (5) that

$$\sigma^{k}_{\lambda\mu} = a^{k}_{l}\ \sigma^{l}_{\lambda\mu}$$

where

$$a^{k}_{l} = \tfrac{1}{2}\sigma'^{k}_{\lambda\mu}\ \sigma^{\lambda\mu}_{l}$$

so that a^k_l are real and

$$a^{k}_{m}\ a^{l}_{n}\ g^{mn} = g^{kl}$$

Therefore a^k_l must be the coefficients of a Lorentz transformation apart from the fact that they may reverse the direction of time

Since the equations (1) and (2) are in a proper covariant form they remain valid for all real transformations of the tensor space and any arbitrary transformations of the spin-space (*cf.* Infeld and Van der Waerden, 1933). However it must be borne in mind that for this general case

$$\epsilon_{0123} = -\sqrt{-g}$$

$$\epsilon^{0123} = \frac{1}{\sqrt{-g}}$$

where g is the determinant of the general g_{ik} matrix. Also ϵ_{12} and ϵ^{12} are no longer 1 but are equal to γ and $\frac{1}{\gamma}$ respectively where γ is a spinor density of weight 1, *i e*, on transformation it gets multiplied by the determinant of the transformation in the spin-space (Infeld and Van der Waerden, 1933) All the results [*e g*, equations (5), (11) and (12)] therefore hold also for the general case which is of importantce in the general theory of relativity

In conclusion let us consider an interesting application of (11) to the Dirac equation of a particle of spin $\frac{1}{2}$ Expressed in terms of spinors it splits up into the following two equations

$$i\,\partial^{a\lambda}\,a_{\lambda} = \chi b^{a} \qquad (30\,a)$$

$$i\,\partial_{a\lambda}\,b^{a} = \chi a_{\lambda} \qquad (30\,b)$$

To these are to be added the corresponding conjugate-complex equations Apart from numerical factors the charge-current-density spinor is given by

$$S_{a\beta} = a_{\alpha}\,a_{\beta} + b_{\alpha}\,b_{\beta} \qquad (31)$$

where a_{α} and b_{β} are the complex-conjugates of a_{α} and b_{β} respectively It is obvious that the charge-density given by (21) is positive definite if the usual representation of σ's is used since in this case σ^{0} is the unit matrix For every other representation of σ's the charge-density is therefore either positive or negative definite according as this representation is obtained from the usual one by a Lorentz transformation without or with the reversal of the direction of time However only the definite character of the charge-density is of importance, the sign being immaterial

Notice that the equations (30) are completely equivalent to the second order equation

$$\partial_{k}\,\partial^{k}\,a_{\lambda} + \chi^{2}\,a_{\lambda} = 0 \qquad (32)$$

which follows from them This becomes obvious if one looks upon (30*a*) as the *definition* of b^{α} Therefore (30) can be replaced by

$$\partial^{k}\,a_{\lambda} = \chi\,a^{k}_{\lambda} \qquad (33\,a)$$

$$\partial^{k}\,a^{k}_{\lambda} = -\chi\,a^{\lambda} \qquad (33\,b)$$

so that

$$b^{a} = i\,\sigma^{a\lambda}_{k}\,a^{k}_{\lambda}$$

(31) now becomes

$$S_{a\beta} = a_{\alpha}\,a_{\beta} + \sigma^{l}_{a\lambda}\,\sigma^{m}_{\beta\mu}\,a^{\lambda}_{l}\,a^{\mu}_{m},\ (a^{\mu}_{m} = a^{\mu}_{m})$$

or

$$S = \tfrac{1}{2}\sigma^{\alpha\beta} S_{\alpha\beta} = \tfrac{1}{2}\sigma^{k,\alpha\beta} a_{\alpha} a_{l} + \tfrac{1}{2}\sigma^{l}_{\lambda\alpha}\sigma^{k,\alpha\beta}\sigma^{\mu}_{\nu\beta} a^{\lambda}_{l} a^{\nu}_{\mu}$$
$$\tfrac{1}{2}\sigma^{l,\alpha\beta} a_{\alpha} a_{l} + \tfrac{1}{2}[\sigma^{\mu}_{\lambda\alpha}(a^{\mu}_{\nu} a^{k\lambda} + a^{\lambda}_{\nu} a^{\mu k}) \sigma^{\nu}_{\lambda\mu} a^{\mu\lambda} a^{\mu k}]$$
$$+ i\epsilon^{klmn} a^{\lambda}_{l} a^{\mu}_{m} \sigma_{n,\lambda\mu} \text{ from (11)} \qquad (34)$$

The equations (33) and (34) are completely equivalent to the usual formulation of the Dirac-equation in the force-free case The definite character of the charge-density is not quite obvious from (34) Equations (33) resemble very much the corresponding equations for a particle of spin 0

However the equivalence of (30) and (33) holds only for the force-free case In case of interaction with an electromagnetic field (30) go over into

$$i\pi^{\alpha\lambda} a_{\lambda} = \chi b^{\alpha} \qquad (35\,a)$$
$$i\pi_{\alpha\lambda} b^{\alpha} = \chi a_{\lambda} \qquad (35\,b)$$

where $\pi^{\alpha\lambda}$ is the spinor corresponding to $\pi_k = \partial_k + ie\phi_k$, ϕ_k being the electromagnetic potentials and e the charge of the particle The second order equation derived from (35) is

$$\pi_{\alpha\lambda}\pi^{\alpha\mu} a_{\mu} + \chi^2 a_{\lambda} = 0$$

Or from (3)

$$\pi_k \pi^{k}_{l} a_{\lambda} + \tfrac{1}{2}(\pi_k \pi_l - \pi_l \pi_k)\sigma^{k}_{\alpha\lambda}\sigma^{l\,\alpha\mu} a_{\mu} + \chi^2 a_{\lambda} = 0$$

which is not the same as that obtained by replacing ∂_k by π_k in (32) Therefore to take electromagnetic interaction into account it is not sufficient to replace ∂^l by π^k in (33) The correct generalisation of (33) in this case is

$$\pi^{k}_{\lambda} a_{\lambda} = \chi a^{k}_{\lambda} \qquad (36\,a)$$

$$\pi_l a^{k}_{\lambda} + \frac{i}{\chi} f^{\mu}_{\lambda} a_{\mu} = -\chi a_{\lambda} \qquad (36\,b)$$

where

$$f^{\mu}_{\lambda} = \tfrac{1}{2} f_{kl}\sigma^{k}_{\lambda\alpha}\sigma^{l\alpha\mu} \text{ and } f_{kl} = \partial_k \phi_l - \partial_l \phi_k$$

The extra term in (36 b) corresponds precisely to the magnetic moment $\frac{e}{\chi}$ of the electron in Dirac's theory The expressions (31) and (34) for the current vector remain unchanged. From (36) it follows that the Dirac equation is *completely equivalent* to the second order equation

$$\pi_k \pi^{k} a_{\lambda} + ie f^{\mu}_{\lambda} a_{\mu} + \chi^2 a_{\lambda} = 0$$

provided the current vector is defined by (34). Equations (36) emphasise the fact that even in the simple case of spin ½ correct electromagnetic interaction cannot be introduced simply by replacing ∂_k by π_k in any arbitrary formulation which is valid for the force-free case

SUMMARY

The σ-symbols are defined by means of the equations (1) and (2) All their properties are deduced from their definition without making use of any explicit representation Certain interesting relations concerning the product of three or more σ's are obtained They are shown to be useful in transforming tensors into spinors and *vice versa*

Directly from (1) and (2) it is deduced that corresponding to every proper Lorentz transformation there exists a spinor-transformation such that the two applied together leave the σ's unchanged The spinor transformation corresponding to the most general proper Lorentz transformation is explicitly given Also the spinor-transformation corresponding to reflection is obtained It is pointed out that since the defining equations (1) and (2) and the relations deduced from them are already in a proper covariant form they can be taken over as such to the general theory of relativity

Finally the Dirac equation for a particle of spin ½ is discussed from a new angle Here only one spinor together with its space-time derivatives (and *not* two spinors) is used to describe the particle It is shown that the Dirac equation is completely equivalent to a second order equation for this single spinor The expression for the charge-current density in terms of this single spinor and its derivatives is obtained In the present formulation correct electromagnetic interaction can be introduced only by the addition of an extra term depending explicitly on the field. This additional term is the one which corresponds to the magnetic moment of the electron

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ON THE MEAN CONSERVING PROPERTY

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1 Introduction

It is the object of this paper to investigate into the general forms of the distribution laws which possess the mean conserving property and arrive at new frequency curves useful for graduation purposes and in tests of significance connected with means in random samples.

The mean conserving property may be defined as follows. Let a variate x be characterised by the probability differential

$$df = \phi(x, \lambda, \mu, \ldots)\, dx \tag{1·1}$$

$\lambda, \mu, \ldots$ being constants which may be called the parameters in the distribution law of x. Let $x_1, x_2, \ldots$ be independent variates from distribution laws of the type (1·1) defined by the sets of parameters given as rows of the matrix

$$\begin{pmatrix} \lambda_1 & \mu_1 & \ldots \\ \lambda_2 & \mu_2 & \ldots \\ \ldots & \ldots & \ldots \end{pmatrix} \tag{1·2}$$

The type (1·1) is said to possess the mean conserving property denoted by

$$\mathrm{M}^{\alpha, \beta, \nu, \ldots}_{\xi, \eta, \zeta, \ldots} \tag{1·3}$$

where $\alpha, \beta, \gamma, \ldots$ and $\xi, \eta, \zeta, \ldots$ are the sets of parameters which have to be kept fixed and can be varied in the distribution laws of $x_1, x_2, \ldots$ if their mean follows the distribution law of the same type as in (1·1) but with the set of parameters

$$(\lambda, \mu, \ldots), \tag{1·4}$$

where $\lambda, \mu, \ldots$ are functions of the number of x's and the elements of the matrix (1·2).

A similar definition holds for the sum conserving property defined by

$$\mathrm{S}^{\alpha, \beta, \gamma, \ldots}_{\xi, \eta, \zeta, \ldots} \tag{1·5}$$

Both (1·3) and (1·5) can be made identical by the introduction of a new constant as a multiplier of x, and the property (1·3) or (1·5) will be referred to as M.

2 Properties of Distribution Laws Satisfying M

From the definition of M we derive the relations

$$\prod_{r=1}^{n} c(t, \lambda_r, \mu_r, \ldots) = c(t, \lambda, \mu, \ldots) \tag{2·1}$$

$$\sum_{r=1}^{n} k_s(\lambda_r, \mu_r, \ldots) = k_s(\lambda, \mu, \ldots) \tag{2·2}$$

where $c(t)$ is the characteristic function corresponding to the distribution law of x and k_s, the sth semi-invariant of x

These simple properties enable us to discover readily whether any distribution law satisfies M when a study of its moments and semi-invariants are made Let us consider the Bessel function populations defined by

$$T_0 e^{-\frac{c}{b}x} |x|^m \left\{ \begin{matrix} \Pi I_m(x) \\ k_m(x) \end{matrix} \right. dx \tag{2·3}$$

where the upper function is taken when $|c| > 1$ and the lower when $|c| < 1$ The moment generating function, in either case, is given by

$$\{f(t, b, c)\}^{m+\frac{1}{2}} = \{(1 - c^2)/(1 - c + tb)\}^{m+\frac{1}{2}} \tag{2·4}$$

Since

$$\prod_{r=1}^{n} \{f(t, b, c)\}^{m_r+\frac{1}{2}} = \{f(t, b, c)\}^{mn+\frac{n}{2}} \tag{2·4}$$

where

$$mn = m_1 + m_2 + \cdots + m_n \tag{2·5}$$

it follows that the sum of n variates from populations of the type (2 3) defined by

$$\begin{pmatrix} b & c & m_1 \\ b & c & m_2 \\ \cdot & & \\ b & c & m_n \end{pmatrix} \tag{2·6}$$

follows the same type defined by

$$(b \quad c \quad n(m + \tfrac{1}{2}) - \tfrac{1}{2}) \tag{2·7}$$

For the Bessel function population defined by

$$T_0 = x^{\frac{m}{2}} e^{-dx} I_m(q\sqrt{x})\, dx \tag{2·8}$$

the sth semi-invariant is given by

$$k_s = (s-1)\,!\,\left\{\frac{(m+1)}{\alpha^s}+\frac{q^2}{4}\,\frac{s}{\alpha^{s+1}}\right\}. \tag{2·10}$$

Hence the sth semi-invariant of $nx = x_1 + x_2 + \ldots + x_n$ where x_i follows the law (2·8) with the parameters α, m_i, q_i is given by

$$k_s = (s-1)\,!\,\left\{\frac{n(n+1)}{\alpha^s}+\frac{nq^2}{4}\,\frac{s}{\alpha^{s+1}}\right\} \tag{2·10}$$

where $$mn = m_1 + m_2 + \ldots + m_n$$

and $$nq^2 = q_1^2 + q_2^2 + \ldots + q_n^2$$

which shows that (2·8) satisfies $M^a_{m,q}$, the set of parameters

$$\begin{pmatrix} \alpha & m_1 & q_1 \\ \ldots & & \\ \alpha & m_n & q_n \end{pmatrix} \tag{2·11}$$

giving the set

$$(\alpha \quad n(m+1)-1 \quad \sqrt{nq}) \tag{2·12}$$

for the distribution of the sum. This result has been obtained by Bose (1937) when m's and q's are the same for all the variables.

If $k_s(r)$, $r = 1, 2, \ldots n$ are the semi-invariants of the variates x_1, x_2, x_n, the distribution laws of which satisfy M, then the semi-invariants of the variate $Z = x_1 + x_2 + \ldots + x_n$ satisfy (2·2). Hence we get the result that *the distribution law of the sum or the mean of any number of independent variates, whose distribution laws satisfy M, also satisfies M.* From this it follows that the distribution law

$$df = c\,e^{-\alpha_1 x}\,x^{n\lambda-1}\sum_{m=0}^{\infty}\frac{m!\,A_m Z^m}{\Gamma(n\lambda+m)} \tag{2·13}$$

$$n\lambda = \lambda_1 + \lambda_2 + \cdots + \lambda_n$$

$$A_m = \frac{d^m}{da^m}\left[\prod_{j=1}^{n}\{1-(\alpha_i-\alpha_j)\,a\}^{-\lambda_j}\right]_{a=0}$$

derived by the author (1942) as the distribution of the sum of n different gamma variates following the laws

$$c\,e^{-\alpha_r x}\,x^{\lambda_r-1}\,dx \tag{2·14}$$

$$r = 1, 2, \ldots, n$$

satisfies M.

It is well known that the distribution law

$$\frac{\alpha^\lambda}{\Gamma(\lambda)}\,e^{-\alpha x}\,x^{\lambda-1}\,dx \tag{2·15}$$

satisfies M^{n}_{λ}. Let the variates $x_1, x_2, \ldots, x_n$ have the probability densities

$$f(x_r, a_r, b_r, \ldots) \qquad (2\cdot16)$$

$$r = 1, 2, \ldots n$$

with the corresponding cumulant functions

$$S(\beta, a_r, b_r, \ldots) \qquad (2\cdot17)$$

If it is known that the distribution of $Z = x_1 + x_2 + \ldots + x_n$ is (2·15) with the cumulant function $-\lambda \log (1 - i\beta/\alpha)$ then by hypothesis we have

$$\sum_{r=1}^{n} S(\beta, a_r, b_r, \ldots) = -\lambda \log (1 - i\beta/\alpha) \qquad (2\cdot18)$$

or

$$\sum_{r=1}^{n} F(\beta, a_r, b_r, \ldots) = -\lambda \qquad (2\cdot19)$$

where $F(\beta) = S(\beta)/\log (1 - i\beta/\alpha)$. Differentiating (2·19) with respect to β we get

$$\Sigma F'(\beta,) a_r, b_r, \ldots) = 0 \qquad (2\cdot20)$$

If this holds for all sets of $a_r, b_r, \ldots$ then we get by setting them equal values for all r, that

$$n F'(\beta, a, b, \ldots) = 0 \qquad (2\cdot21)$$

or

$$S(\beta, a, b, \ldots) = c \log (1 - i\beta/\alpha) \qquad (2\cdot22)$$

where c must necessarily be negative if the right-hand side is to represent a cumulant function. Hence $f_r(x_r, a_r, b_r, \ldots)$ is of the gamma type. So we get the result that *if the sum of* n *independent variates drawn from* n *different populations of the same type (the mathematical form remaining the same and the parameters may be varying) follows the gnmma type distribution law, then the above original populations also belong to the gamma type.* As a result of this we get the necessary and sufficient condition for the sum of n into pendent observations from a population to follow the gamma type is that the population itself is of the gamma type. Also it easily follows that *if the sum of two variates of which one follows the gamma type, is distributed in the gamma type, then the other variate also follows the gamma type.*

3. Differential Equation Satisfied by the Characteristic Function

When all the n variates are drawn from the same population, we have, if $c(t)$ represents the characteristic function of the distribution in the population satisfying M,

$$\{c(t, \lambda', \mu', \ldots)\}^{n} = c(t, \lambda, \mu, \ldots). \qquad (3\cdot1)$$

Taking logarithms and representing $\log c(t)$ by $\psi(t)$ we get

$$n\psi(t, \lambda', \mu', \ldots) = \psi(t, \lambda, \mu, \ldots). \tag{3·2}$$

Starting from $\psi(t, \lambda', \mu', \ldots)$ we can form the differential equation satisfied by ψ under some analytical conditions by eliminating the constants $\lambda', \mu', \ldots$ The order of the differential equation is, in general, equal to the number of constants eliminated. Since $\psi(t, \lambda, \mu, \ldots)$ also should satisfy this equation, we require that ψ and $n\psi$ should both satisfy the differential equation for ψ If the differential equation satisfied by ψ is

$$D(\psi, \psi' \ldots) = 0 \tag{3 3}$$

then

$$D(n\psi, n\psi', \ldots) = 0 \tag{3·4}$$

which shows that D must be homogeneous in $\psi, \psi', \psi'', \ldots$ the homogeneity of $D(x, y, \ldots)$ being defined as

$$D(ax, ay, \ldots) = f(a)\, D(x, y, \ldots) \tag{3 5}$$

The differential equation (3 4) may be denoted by $D_H = 0$. Hence we get the results that *the semi-invariant generating function corresponding to a distribution law satisfying M satisfies a homogeneous differential equation homogeneity being defined as in* (3·5).

From the above differential equation $D_H = 0$, we can derive the differential equation satisfied by $c(t)$ by making the substitutions

$$\psi = \log c, \ \psi' = c'/c \text{ etc.} \tag{3 6}$$

If the differential equation $D_H = 0$ arising out of the probability differential $\phi(x)\,dx$ is homogeneous then the differential equation arising out of the probability differential $\chi(a)\, e^{ax}\, \phi(x)\, dx$ is also homogeneous which shows that the property M is conserved by the multiplication of the distributive law by an exponential factor.

We shall now consider some distribution laws obtained by inversion from $D_H = 0$. The simplest case is when the order of $D_H = 0$ is one, in which case the differential equation becomes

$$\frac{\psi'}{\psi} = f(t) \text{ (an arbitray function)} \tag{3·7}$$

which gives the solution

$$\psi = \lambda\, e^{\phi(t)} \text{ where } \phi(t) = \int f(t)\, dt \tag{3·8}$$

and $c(t) = e^{\psi}$. If $e^{\phi(t)}$ admits an expansion in series we get

$$c(t) = e^{\lambda\left(a_0 + a_1 \frac{t}{\lfloor 1} + a_2 \frac{(t)^2}{\lfloor 2} + \cdots\right)}$$

which shows the λa_1, λa_2, ... are the semi-variants of the distribution. In particular if a_1, a_2, .. are the semi-invariants for any distribution law then na_1, na_2, . . are the semi-invariants for the sum of n independent observations from the above distribution. This gives the result that *the distribution law of the sum or mean of a number of observations from any distribution law with finite semi-invariants satisfies M* The functional form of the distribution law may change with n but may be capable of being represented by a general type of function. Thus we get a huge class of distribution laws satisfying M.

4. Measures of Departure from M

Given the probability density $\phi_1(x, \lambda, \mu, \ldots)$ of a variate x, we can, in general, replace the constants $\lambda, \mu, \ldots$ by an equivalent number of semi-invariants of suitable orders so that $\phi_1(x, \lambda, \mu, \ldots)$ may be written as $\phi(x, k_1, k_2, \ldots)$ where $k_1, k_2, \ldots$ are the first, second, etc., semi-invariants. Let the cumulant generating function be $k(t, k_1, k_2, \ldots)$. Then the cumulant generating function of the mean of n observations is $nk(t, k_1, k_2, \ldots)$. Let $R(t, n, k_1, k_2, \ldots)$ be defined by

$$n k\left(\frac{t}{n}, k_1, k_2 \ldots\right) = k(t, k_1, k_2/n, \ldots) + R(t, n, k_1, \ldots) \tag{4·1}$$

When the distribution law satisfies M, R vanishes If not, it can be written, when it admits expansion, as

$$R(t, n, k_1, \ldots) = \sum_{\rho=s}^{\infty} \frac{a_\rho}{\rho!} t^\rho \tag{4·2}$$

where s depends on the number of constants involved in the distribution law of x. Taking the exponentials in (4·1) we get

$$\left[\sum_{\rho=s}^{\infty} \frac{a_\rho}{\rho!} t^\rho\right] \tag{4·3}$$

On taking the integral transform we get the probability density $S(z)$ of the mean as

$$S(z) = \phi(z, k_1, k_2/n, \cdots) + \sum^{\infty} \frac{b_\rho}{\rho!} \frac{d^\rho}{dz^\rho} \phi(z). \tag{4·4}$$

The expression consists of two portions The second part vanishes when M holds and measures the departure from M when M does not hold. The considerations of replacing $S(z)$ by $\phi(z, k_1, k_2/n, \ldots)$ depend upon the magnitude of this measure. It is proposed to study the effect of the departure from M when n increases and also to consider the effect of replacing $\phi(z, k_1, k_2/n)$ by the normal approximation.

5 Series in Orthogonal Polynomials

Let $M(\alpha)$ be the *m.g.f.* of a variate whose distribution law satisfies M and $f(\alpha)$ any arbitrary function. If

$$G_1 = M_1(\alpha) \sum_{r=0}^{\infty} \frac{a_r}{r!} \{f(\alpha)\}^r \tag{5·1}$$

$$G_2 = M_2(\alpha) \sum_{r=0}^{\infty} \frac{b_r}{r!} \{f(\alpha)\}^r \tag{5·2}$$

are the *m.g.f.*'s of x_1 and x_2 following the distribution laws

$$\phi(x, \lambda_1, \mu_1, \ldots)\, dx \tag{5·3}$$

$$\phi(x, \lambda_2, \mu_2, \ldots)\, dx \tag{5·4}$$

then the *m.g.f.* of $z = x_1 + x_2$ is

$$G = G_1 G_2 = M_1 M_2 \sum_{l=0}^{\infty} \sum_{r+s=l} \frac{a_r}{r!} \frac{b_s}{s!} f^l \tag{5·5}$$

$$= M_3 \sum_{l=0}^{\infty} \frac{c_l}{l!} f^l.$$

The functional form of G will be same as that of G_1 and G_2 if the same holds for c_l and a_r and b_r *i.e.*, a_r satisfies the recurrence relation

$$\sum_{r+s=l} \frac{a_r b_s}{r!\, s!} = \frac{c_l}{l!} \tag{5·6}$$

where b_r and c_l are of the same form as a_r differing only in the parameters involved in them If (5·6) holds then by successive applications we can show that

$$G = G_1 G_2 \ldots . G_n \tag{5·7}$$

has the same functional form as G_1. By a suitable selection of $M(\alpha)$ and $f(\alpha)$ we can get several distribution laws satisfying M.

Let $M(\alpha) = (1-\alpha)^{-p}$ and $f(\alpha) = \alpha/(1-\alpha)$

Since $(1-\alpha)^{-p}\, \alpha^r/(1-\alpha)^r$

$$= \frac{(-1)^r \alpha^r}{p(p+1)\cdots(p+r-1)} \frac{d^r}{d\alpha^r} (1-\alpha)^{-p}$$

i.e., the *m.g.f.* corresponding to

$$\frac{\Gamma(p)}{\Gamma(p+r)} L_r(x, p)\, \phi(x) \tag{5·8}$$

where $\phi(x) = e^{-x} x^{p-1}/\Gamma(p)$ and $L_r(x, p) = \left(\frac{-d}{dx}\right)^r x^r\, \phi(x)$ we see that $(1-\alpha)^{-p}\left(a_0 + \frac{a_1}{1!} f(l) + \cdots\right)$ is the *m.g.f.* of

$$\gamma(x) = \phi(x) \sum_{r=0}^{\infty} \frac{a_r}{r!} \frac{\Gamma(p)}{\Gamma(p+r)} L_r(x, p) \tag{5·9}$$

where a_r satisfies (5·6). This is a series in Lagurre's polynomials satisfying M.

Let $M(\alpha) = e^{\alpha' \sigma^2}$, $f(\alpha) = \alpha$ We get that

$$e^{\alpha' \sigma^2} \sum_{r=0}^{\infty} \frac{a_r}{r!} \alpha^r \tag{5·10}$$

is the *m.g.f.* of

$$\psi(x) = \text{const.}\, e^{-\frac{x^2}{2\sigma^2}} \left(a_0 + \frac{a_1}{1!} H_1 + \frac{a_2}{2!} H_2 + \cdots \right), \tag{5·11}$$

where $$H_p = e^{\frac{x^2}{2\sigma^2}} \frac{d^p}{dx^p} e^{-\frac{x^2}{2\sigma^2}},$$

which is a series in Hermite polynomials satisfying M if a_r satisfies (5·6) By suitable selections of $M(\alpha)$ and $f(\alpha)$ we can obtain the development of probability functions satisfying M in a series of Bessel functions (Neumann's expansion) involving $J_n(x)$, Hypergeometric and other suitable functions. These are omitted here as they are not of direct interest in graduation or tests of significance

6. Some Special Series

A series of the form

$$c\, e^{-\alpha x}\, x^m \sum \frac{a_r}{r!} x^r \tag{6·1}$$

is of special interest for the gamma type distribution occurs as a generating function. We shall investigate into the nature of a_r so that (6 1) satisfies M. If x and y follow the type (6·1) with the parameters

$$\begin{pmatrix} \alpha & \lambda & m_1 & p_1 & \cdot & \cdot \\ \alpha & \lambda & m_2 & p_2 & \cdots & \end{pmatrix} \tag{6·2}$$

then the distribution of $z = x + y$ is given by

$$c'\, e^{-\alpha z}\, dz \frac{d}{dz} \iint_{\Omega} \sum \sum \frac{a_r}{r!} \frac{b_s}{s!} x^{m_1 + \lambda r}\, y^{m_2 + \lambda s}\, dx\, dy \tag{6·3}$$

where the integral is over the domain Ω defined by $x > 0$, $y > 0$ and $x + y < z$. This becomes apart from const. $e^{-\alpha z}\, dz$,

$$\begin{aligned} &\frac{d}{dz} \sum \sum \frac{a_r}{r!\, \Gamma(m_1 + \lambda r + 1)} \frac{b_s}{s!\, \Gamma(m_2 + \lambda s + 1)} \\ &\qquad \times \frac{z^{m_1 + m_2 + \lambda (r+s) + 2}}{\Gamma(m_1 + m_2 + \lambda (r+s) + 3)} \\ &= \sum \sum \frac{a_r' b_s'}{r!\, s!\, \Gamma(m_1 + m_2 + \lambda (r+s) + 2)} \end{aligned} \tag{6·4}$$

where

$$a_r' = a_r/\Gamma(m_1 + \lambda r + 1)$$

$$b_s' = b_s/\Gamma(m_2 + \lambda s + 1)$$

The distribution of Z now becomes

$$c^n e^{-ax}\, dz \sum_{l=0}^{\infty} \frac{A_l'}{\Pi} \frac{z^{m_1 + m_2 + \lambda l + 1}}{\Gamma(m_1 + m_2 + \lambda l + 1)}$$

$$= c = e^{-ax}\, dz \sum_{l=0}^{\infty} \frac{A_l}{\Pi} z^{m \quad \lambda l}$$

where $m = m_1 + m_2 + 1$ and

$$A_l\, \Gamma(m_1 + m_2 + \lambda l + 1) = A_l' = l\,! \sum_{r+s=l} \frac{a_r'\, b_s'}{r\,!\, s\,!}$$

which shows that (6·1) satisfies M if a'_r satisfies (5·6) The method of proof can be extended to the sum of n variates. Some particular forms of a'_r give rise to important distribution laws.

(*a*) $a'_r = q^r$ then (6·1) satisfies $M^{a,\lambda}_{m,q}$

(*b*) $a'_r = \Gamma\left(\frac{m+1}{\lambda} + r\right)$ satisfies $M^{a,\lambda,q}_{m}$

(*c*) $a'_r = \Gamma(p+r)\, q^r$ satisfies $M^{a,\lambda,q}_{p,m}$

(*d*) $a'_r = \sum_{\gamma_1+\gamma_2+\ldots=r} \Gamma(p_1+r_1)\, q_1^{r_1}\, \Gamma(p_2+r_2)\, q^{r_2}$ satisfies $M^{a,\lambda,q_1,q_2,\ldots}_{m,p_1,p_2,\ldots}$

The solutions for (*a*), (*b*), (*c*) and (*d*), in the special case $\lambda = 1$, become

(*a*) $c\, e^{-dx} \sum^{m} x^{\frac{}{}} I_m(q\sqrt{x})$

(*b*) $c\, e^{-ax}\, x^m\, I_m(qx)$

(*c*) $c\, e^{-ax}\, x^m\, {}_1F_1(p, m+1, qx)$

(*d*) The distribution (2·13) of Section 2.

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AN ELECTRICAL AIRPLANE C.G. POSITION INDICATOR*

By P. Nilakantan

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Introduction

Although several types of Airplane C G Determinators are known which work on the mechanical principle of the lever just as the common balance, their manipulation is rather cumbersome and the devices themselves are not very handy In the present paper an electrical circuit is described which is capable of indicating the centre of gravity position of an airplane for any arbitrary manner of loading after a few adjustments requiring very little skill. The design of the circuit for the case of a typical airplane is explained with the help of a numerical example This should serve the purpose of further clarifying the theoretical considerations

Basic Principle

The position of the centre of gravity of an airplane in the horizontal plane and at the normal attitude corresponding to the level flight condition at cruising speed, is determined by the relation,

$$x = \frac{\sum_{i=0}^{i=n} w_i x_i}{\sum_{i=0}^{i=n} w_i} = \frac{\sum_{i=0}^{i=n} m_i}{\sum_{i=0}^{i=n} w_i}, \qquad (1)$$

where w_i is the weight of load item i, and x_i is the corresponding moment arm measured from any convenient centre of gravity datum point, the total number of items being n A simple electrical analogy of the division indicated in relation (1) may be envisaged by considering a voltage that is proportional to the algebraic sum of the moments, applied at the ends of a resistance that is proportional to the sum of the weights. the resulting current in the resistance will be proportional to the distance of the centre of gravity of the airplane from the datum point. This is the basic principle of the centre of gravity indicator.

Theory of the Electrical Circuit

The arrangement of an electrical circuit in order that the conditions mentioned above may be realized in practice is shown in Fig. 1.

* Patents applied for.

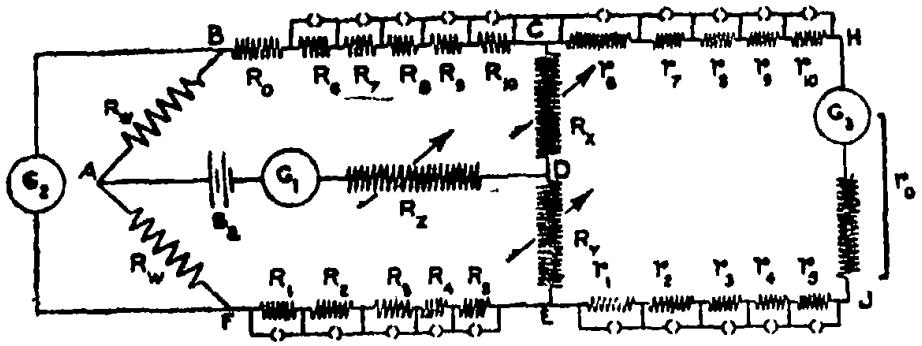


FIG 1

The resistances, R_0, R_1, R_2, ... R_{10} shown in the figure, are made proportional to the moments m_0, m_1, m_2, ... m_{10} of the airplane weight empty and the altogether 10 items of the disposable load respectively (n is arbitrarily assumed to be 10 in this case) Similarly, the resistances r_0, r_1, ... r_{10} are made proportional to the corresponding weights w_0, w_1, ... w_{10} respectively All the positive moments (clockwise) are included in the arm ABC while all the negative moments (anti-clockwise) are in the arm AFE of the electrical circuit. The R_w's are two equal resistances. G_1 and G_2 are current meters while G_3 is a sensitive galvanometer G_3 has its zero reading in the middle of the scale

The rheostats R_x and R_y may be so adjusted that G_3 reads zero. then the currents in the arms ABC and AFE are equal The rheostat R_z could then be adjusted such that the current registered by G_1 has a specific value say c_1. c_1 is an instrument constant and its significance will become evident later. The currents in the arms ABC and AFE of the circuit will have the same value, say c_2, which again will be equal to $\frac{1}{2}c_1$ This is due to the fact that the two resistances R_w are equal and G_3 reads zero. The currents in the arms CD, DE, and CHJE will be equal to $c_2 + c_3$, $c_2 - c_3$, and c_2 respectively. Applying the well-known law of electrical networks, the following relations are obtained:—

$$c_2 R_A - c_2 R_B - c_2 r = 0 \qquad (2)$$

$$(c_2 + c_3) R_X - (c_2 - c_3) R_Y + c_2 r = 0 \qquad (3)$$

$$c_2 (R_w + R_A) + (c_2 + c_3) R_X = c_2 (R_w + R_B) + (c_2 - c_3) R_Y = E_{B_3} - (R_{G1} + R_z) c_1 = E \text{ say} \qquad (4)$$

where,

$$R_A = R_0 + R_6 + R_7 + R_8 + R_9 + R_{10},$$

$$R_B = R_1 + R_2 + R_3 + R_4 + R_5,$$

$$r = r_0 + r_1 + r_2 \ldots\ldots + r_{10};$$

R_{G_1} is the resistance of G_1 and

r_0 includes the resistance of G_2.

From equations (2), (3) and (4), the following relations are easily obtained, namely,

$$c_2 = \frac{(R_A - R_B)\, c_2}{r} \tag{5}$$

$$R_X = \left\{\frac{E}{c_2} - (R_w + R_A)\right\} \frac{r}{r + (R_A - R_B)} \tag{6}$$

$$R_Y = \left\{\frac{E}{c_2} - (R_w + R_B)\right\} \frac{r}{r - (R_A - R_B)} \tag{7}$$

Although the value of c_1 and therefore of c_2 also may be arbitrarily decided upon initially in order to suit the most advantageous design of the instrument, the absolute values of R_X and R_Y are not uniquely determined; their values will depend upon the values of E and R_w. The relative values of R_X and R_Y are, however, fixed by the values of R_A, R_B and r, according to the relation,

$$\frac{R_A - R_B}{r} = \frac{R_Y - R_X}{R_X + R_Y + r} \tag{8}$$

The operations performed may now be considered in the light of the above equations. The essential object of the manipulations has been to make c_2 equal to $\frac{1}{2}c_1$. The relation (5) then directly gives the answer to the problem. For, $(R_A - R_B)$ corresponds to the algebraic sum of the moments and r corresponds to the total weight of the airplane, c_2 being an instrument constant. Hence, c_2 is always proportional to $\frac{(R_A - R_B)}{r}$.

Assuming the resistances to be so chosen that 1 ohm of the resistances R_j is equivalent to a inch-pounds and that 1 ohm of the r_i's is equivalent to b pounds, we have then from equation (5),

$$\frac{c_2}{c_2}\,\frac{a}{b} = \frac{(R_A - R_B)}{r}\,\frac{a}{b} \text{ inches} \tag{9}$$

In other words, if c_2, read in milli-amperes, is multiplied by the factor $\frac{a}{b}\,\frac{1}{c_2}$ in which c_2 is also in milli-amperes, we get directly the C.G. position in inches from the datum point. For practical purposes G_2 can be calibrated in inches of C.G. position fore and aft. Since c_1 is an instrument constant, its value read on G_1 may also be indicated by an index mark on the dial of the instrument.

Some Practical Considerations

It is not the purpose here to go into minute details of design of the circuit for any airplane. But attention may be drawn to some points of practical interest by considering the case of a typical airplane of 6,000 lbs. gross weight The weight and moment data of the airplane are given in Table I below.

Table I

Item	Weight W_i (lbs)	Moment arm X_i (inches)	Moment m_i (inch—lbs)
Airplane weight empty	4000	0	0
Pilot	170	−35	−5950
1st Passenger	170	5	− 850
2nd ,,	170	− 5	− 850
3rd ,,	170	25	4250
4th ,,	170	25	4250
5th ,,	170	55	9350
6th ,,	170	55	9350
Fuel (full)	450	10	4500
Cargo (full)	360	90	32400
Total	6000		56450

The datum point in the horizontal plane for the measurement of moment arms has been chosen for convenience as that corresponding to the centre of gravity position of the airplane weight empty In fact, it may be preferable to choose the datum point given by the manufacturer himself and the centre of gravity limits specified in the *Airplane Manual* with reference to this datum point may be indicated on the dial of G_2 This however, is only a design detail.

Table II

Item No i	Item Description	Resistance r_i (ohms)	Resistance R_i (ohms)
0	Airplane weight empty ..	400	0
1	Pilot ..	17	5 95
2	1st Passenger	17	85
3	2nd ,, ..	17	85
4	3rd ,, ..	17	4 25
5	4th ,, .	17	4·25
6	5th ,, .	17	9 35
7	6th ,, ..	17	9 35
8	Fuel ..	*0–45	*0–4 5
9	Cargo .	*0–36	*0–32·4

Adjustable in fractions ¼, ½ and ¾ of full value

The electrical circuit for the airplane under consideration may be designed such that 1 ohm of the R_i's is equivalent to 1000 inch-pounds and 1 ohm of the r_i's to 10 pounds weight. The actual values of r_i and R_i for the various items are then as given in Table II.

The value of c_1 is fixed at 20 milli-amperes. Hence c_2 will be 10 milli-amperes. The multiplying factor is 10 when c_2 is read in milli-amperes, in order to get the C.G. position in inches. For the battery a two-volt accumulator cell may be used

Considering the case of the fully loaded airplane, we have

$R_A = 64{\cdot}1\ \Omega$

$R_B = 7{\cdot}65\ \Omega$, and

$r = 600\ \Omega$

Hence $c_3 = {\cdot}941\ m\,a$. This evidently corresponds to a C G. position of 9 41 inches aft of the datum point If the R_w's are each equal to $10\ \Omega$, then it may be easily shown that, corresponding to a value of $(R_{G_1} + R_Z) = 50\ \Omega$,

$R_X = 23{\cdot}7\ \Omega$, and

$R_Y = 90{\cdot}8\ \Omega$,

from equations (4), (6) and (7)

It may also be shown that if R_X is initially kept at some arbitrary value, say $20\ \Omega$, the appropriate values of R_Y and $(R_{G_1} + R_Z)$ are $86{\cdot}48\ \Omega$ and $52\ \Omega$ respectively

The above considerations show that the manipulation of the instrument is a very simple matter and often only R_Y and R_Z need be adjusted.

By means of the short-circuiting plugs provided, any arbitrary manner of loading of the airplane may be reproduced on the circuit (see Fig 1), and the C.G position in inches read directly on the dial of G_3 after two or three adjustments.

SUMMARY

The theory of the electrical circuit of an Airplane C.G. Position Indicator has been developed. The practical application of the circuit to the case of a typical airplane has been demonstrated with the help of a numerical example.

THE ACTION OF HEXAMETHYLENE TETRAMINE ON PHENOLS AND THE METHYL ESTERS OF PHENOL CARBOXYLIC ACIDS

Part II. The Synthesis and Study of Methyl-2 : 3 4 Trihydroxy-5-formyl-benzoate

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2 : 4-Dihydroxy-5-formyl benzoic acid was synthesised by Desai and Radha,[1] by the action of hexamethylene tetramine on methyl-β-resorcylate in glacial acetic acid. The same reaction has now been extended to some phenols and to methyl-2 · 3 . 4-trihydroxy-benzoate

Methyl-2 · 3 . 4- trihydroxy-benzoate on formylation with hexamethylene tetramine in glacial acetic acid, yielded methyl-2 3 . 4- trihydroxy-5-formyl-benzoate, which was characterized by the preparation of its 2 4-dinitro-phenyl hydrazone, 4-nitrophenyl-hydrazone and semicarbazone derivatives.

The ortho-hydroxy-aldehydic structure of the formyl ester was proved by the preparation of the coumarin derivatives of the formyl ester with ethyl acetoacetate and ethyl malonate by the Knoevenagel condensation Thus, with ethyl acetoacetate, the ester gave methyl-7 · 8-dihydroxy-3-acetyl-coumarin-6-carboxylate and with ethyl malonate, it afforded ethyl-7 · 8-dihydroxy-6-carbomethoxy coumarin-3-carboxylate

Clemmensen reduction of the formyl ester afforded methyl-2 . 3 4-trihydroxy-5-methyl benzoate

Hydrolysis of the ester gave the corresponding aldehydo-acid, 2 . 3 4-trihydroxy-5-formyl benzoic acid, which when subjected to decarboxylation underwent decomposition

On Perkin's acetylation and condensation with bromacetic ester, the formyl ester was recovered unchanged.

Attempts were made to formylate orcinol, methyl-*p*-orsellinate, phloroglucinol, resacetophenone, methyl-resaceto-phenone carboxylate, hydroquinone, 1 . 3 . 5-triacetoxy benzene, methyl-α-resorcylate, γ-resorcylic acid, and methyl-γ-resorcylate. Of these, orcinol, methyl-*p*-orsellinate, phloroglucinol, γ-resorcylic acid and methyl-γ-resorcylate gave amorphous, yellowish-brown, high-melting compounds which contained appreciable amount

of nitrogen. Resacetophenone and hydroquinone gave oily products which did not solidify, whereas in the case of methyl resacetophenone carboxylate and 1.3:5-triacetoxy benzene, no reaction took place and the starting compounds were recovered. Methyl-*a*-resorcylate afforded a yellowish, nitrogenous amorphous, and high-melting compound which reacted with dinitrophenyl-hydrazine, indicating the presence of traces of the aldehyde compound.

Experimental

Formylation of methyl-2:3:4-trihydroxy benzoate· Methyl-2·3:4-trihydroxy-5-formyl benzoate A mixture of methyl-2.3·4-trihydroxy benzoate (12 g.), hexamethylene tetramine (36 g), glacial acetic acid (60 c c.) and sodium bi-sulphite (6 g.) was heated on a water-bath for 8–10 hours and for further 3–4 hours after the addition of dilute hydrochloric acid (130 c.c., 1:1) An orange-red compound, which separated, was filtered off The filtrate was salted and both the filtrate and the orange-red solid, were extracted with ether, when a pale-yellow mass was obtained on the evaporation of the ether. On crystallizing from dilute hot alcohol, whitish, shiny, microcrystals were obtained (6 7 g), m p 169–70°. (Found: C, 51·4; H, 4·3; $C_8H_8O_6$ requires C, 50 9; H, 3·8 per cent) It gave a dark green colouration with alcoholic ferric chloride

The 2:4-dinitrophenyl hydrazone of the formyl ester prepared in the usual manner and crystallized from glacial acetic acid in tiny orange-red crystals, melted at 295° (Found N, 14·2, $C_{14}H_{12}O_8N_4$ requires N 14·3 per cent.)

The 4-nitrophenyl hydrazone of the ester, prepared by the usual method and crystallized from acetic acid in orange red micro-crystals, melted at 285° with decomposition. (Found. N, 12·1, $C_{10}H_{13}O_4N_3$ requires N, 12·5 per cent.)

The semicarbazone of the ester, prepared in the usual manner, gave colourless micro-crystals, m.p. 238° (Found. N, 15·6; $C_{10}H_{11}O_6N_3$ requires N, 15·7 per cent)

Methyl-7: 8 dihydroxy-3-acetyl-coumarin-6-carboxylate.—Piperidine (3 drops) was added to a mixture of the formyl ester (1 g.) and ethyl acetoacetate (1 g.) dissolved in pyridine (10 c.c), and the mixture was heated at 100° for one hour. The solid obtained on the addition of dilute hydrochloric acid was triturated with 2 N-potassium hydroxide solution to remove the unreacted formyl ester. The insoluble solid obtained crystallized in greyish-white needles from dilute hot alcohol, m.p. 263–64°. (Found. C, 56·3; H, 4·0; $C_{13}H_{10}O_7$ requires C, 56·1; H, 3 6 per cent)

Ethyl-7 : 8-dihydroxy-6-carbomethoxy-coumarin-3-carboxylate —Piperidine (3 drops), was added to a mixture of the formyl ester (1 g) and ethyl malonate (1 g) dissolved in pyridine (10 c.c) and the mixture was heated on boiling water-bath for two hours. The solid obtained on acidifying with dilute hydrochloric acid, crystallized from hot alcohol in colourless needles (0·25 g), m p. 245–47°. (Found· C, 54 2; H, 3 5, $C_{14}H_{12}O_8$ requires C, 54 5; H, 3·8 per cent).

Methyl-2 : 3 : 4-trihydroxy-5-methyl benzoate.—The formyl ester (1 5 g.), dissoved in hot alcohol (20 c.c), was gradually added to a mixture of zinc amalgam (prepared from 20 g. of zinc dust according to Robinson and Shah[2]) and dilute hydrochloric acid (50 c c, 1 · 1) at 100°, more alcohol being added to keep the ester in solution whenever it was necessary. After one hour, concentrated hydrochloric acid (10 c c.) was added and the heating continued for a further half hour The hot liquid, after filtration deposited shining, greyish micro-crystals, m p. 178–79°, on cooling. The ethereal extract of the zinc amalgam gave a further yield of the same compound Total yield (0·8 g.). (Found: C, 54·3, H, 5 0; $C_8H_{10}O_5$ requires C, 54 5, H, 5·0 per cent.) It did not react with 2 4-dinitrophenyl hydrozine and the mixed melting point with the formyl ester was 130–40°

2 . 3 : 4-trihydroxy-5-formyl-benzoic acid —The aldehydo-ester (0·7 g.) was dissolved in sodium hydroxide solution (20 c c, 10%) and heated on a water-bath for 2–3 hours. The hot solution was filtered and acidified with hydrochloric acid. The solid was purified through sodium-bi-carbonate solution and crystallized from very dilute alcohol in colourless micro-crystals, m p. 221–22°, (Found· C, 48·7; H, 3 0; $C_8H_6O_6$ requires C, 48 5; H 3·0 per cent)

The foregoing formyl acid (0·2 g.) was heated in a hard glass sealed tube with water (10 c c) and hydrochloric acid (1 c c) for 5–6 hours at 160–70°. The dark brown solid purified through sodium bicarbonate solution did not give tests for the aldehydo group with 2 : 4-dinitro-phenyl-hydrazine.

Summary

1. Methyl-2 · 3 : 4-trihydroxy benzoate was formylated by the action of hexamethylene-tetramine in glacial acetic acid and methyl-2 : 3 : 4-trihydroxy-5-formyl benzoate was obtained. Several derivatives of the formyl ester were prepared and the structure established.

2. Formylation of several hydroxy compounds was also attempted.

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THE ACTION OF HEXAMETHYLENE TETRAMINE ON PHENOLS AND THE METHYL ESTERS OF PHENOL CARBOXYLIC ACIDS

Part III. The Synthesis and Study of Methyl-2-hydroxy-1-formyl-3-naphthoate

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In continuation of our previous work,[1] the formylation of phenols and phenol carboxylic esters, has now been extended to some methyl esters of naphthol-carboxylic acids, namely, methyl-2-hydroxy-3-naphthoate and methyl-2-hydroxy-1-naphthoate.

Methyl-2-hydroxy-3-naphthoate on formylation with hexamethylene tetramine in glacial acetic acid, yielded a mixture of methyl-2-hydroxy-1-formyl-3-naphthoate and 2-hydroxy-1-formyl-3-naphthoic acid. The structure of the latter was proved by the hydrolysis of the former and the subsequent hydrolysis product on decarboxylation underwent simultaneous deformylation to give β-naphthol. The formyl ester and the acid both were characterized by their functional derivatives, like 2. 4-dinitro-phenyl hydrazones and semicarbazones The ortho-hydroxy aldehydic structure was proved by the formation of coumarin derivatives, *viz.*, 3-acetyl-10 carbmethoxy-β-naphtha-α-pyrone and 3-carbethoxy-10-carbmethoxy-β-naphtha-α-pyrone by the knoevenagel condensation of the formyl ester with ethyl acetoacetate and ethyl malonate respectively. On subjecting it to Perkin's acetylation it yielded, 10-carbmethoxy-β-naphtha-α-pyrone while condensation with ethyl bromoacetate gave, ethyl-1-formyl-3-carbmethoxy-naphthalene-2 6-acetate, which on treating with sodium ethoxide in absolute alcohol, gave a coumarone derivative, ethyl-β-naphtha-furane-9-carboxy-2-carboxylate. Clemmensen reduction of the formyl ester with different solvents, under different conditions, gave different products. Methyl alcohol as the solvent afforded methyl-2-hydroxy-1-methyl-3-naphthoate, which on hydrolysis gave the corresponding acid, 2-hydroxy-1-methyl-3-naphthoic acid, which could not be decarboxylated.

However, when glacial acetic acid is used as the solvent and the reaction mixture heated for different lengths of time, two more compounds, which are being studied, are obtained.

Methyl-2-hydroxy-1-naphthoate could not be similarly formylated.

Experimental

Formylation of methyl-2-hydroxy-3-naphthoate.—Methyl-2-hydroxy-1-formyl-3-naphthoate and 2-hydroxy-1-formyl-3-naphthoic acid. A mixture of methyl-2-hydroxy-3-naphthoate (10 g.), hexamethylene tetramine (30 g) and glacial acetic acid (50 c.c.) was refluxed on a water-bath for 5–6 hours and further for three hours, after the addition of hydrochloric acid (100 c.c., 1 : 1). The solid which separated was filtered, washed and treated with sodium bicarbonate solution (5%). The insoluble solid was washed with water and was crystallized from glacial acetic acid in very shiny, yellow plates, m.p. 146–47°. (Found: C, 67·6; H, 4·0, $C_{13}H_{10}O_4$ requires C, 67·8, H, 4·3 per cent.) It gave an intense blue colouration with alcoholic ferric chloride.

The sodium bicarbonate-soluble portion was acidified with dilute hydrochloric acid, and the solid obtained was crystallized from very dilute alcohol in yellow micro-crystals, m.p. 218°–20° Mixed melting point with 2-hydroxy-1-formyl-3-naphthoic acid (described later) was undepressed. (Found: C, 63·6, H, 4·0, $C_{12}H_8O_4$ $\frac{1}{2}H_2O$ requires C, 64·0, H, 4·0 per cent.). It gave effervescence with sodium bicarbonate solution and a blue colouration with alcoholic ferric chloride

The p-*nitrophenyl-hydrozone* of the formyl ester prepared as usual, crystallized in orange-red microcrystals from glacial acetic acid, m.p. 295° (decomp.) (Found: N, 11·2, $C_{19}H_{15}O_5N_3$ requires, N, 11·5 per cent.)

The 2·4-*dinitrophenyl-hydrazone* prepared in the usual manner crystallized in orange-red crystals from glacial acetic acid, m.p. 298° (decomp.). (Found: N, 13·2; $C_{18}H_{14}O_6N_4$ required N, 13·6 per cent.)

The semicarbazone prepared as usual crystallized from alcohol in shiny, pale-yellow micro-crystals, m.p. 238° (Found: N, 14·5; $C_{14}H_{13}O_4N_3$ requires N, 14·6 per cent.)

3-*carbethoxy*-10-*carbmethoxy*-β-*naphtha*-α-*pyrone*.—Piperidine (4 drops) was added to a mixture of the formyl ester (0·9 g.) and ethyl malonate (1 g.) dissolved in pyridine (10 c.c.) and the mixture was heated on a water-bath for two hours. The solid obtained on acidifying with hydrochloric acid was crystallized from hot alcohol in shiny, greenish-yellow micro-crystals, m.p.

157-58°. (Found. C, 66 2; H, 4 1, $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3 per cent.)

3-Acetyl-10-carbmethoxy-β-naphtha-α-pyrone.—A mixture of the formyl-ester (0·5 g.), ethyl acetoacetate (0 6 g) and piperidine (3–4 drops) was heated on a water bath for two hours During heating, very long yellow needles separated, which were filtered, washed with hydrochloric acid and water and dried, m p. 240–41°. (Found: C, 68·6; H, 4 1; $C_{17}H_{12}O_6$ requires C, 68·9; H, 4 0 per cent.)

Ethyl-1-formyl-3-carbmethoxy-naphthalene-2-o-acetate.—The formyl ester (0·9 g) was dissolved in acetone (100 c.c.), ethyl bromo acetate (1 g.) and anhydrous potassium carbonate (2 g) were then added to the mixture and refluxed on a water-bath for 10 hours The excess of ethyl bromoacetate and acetone were driven off in a current of air, after filtering off the potassium carbonate, and the flaky mass obtained was crystallized from hot dilute alcohol in long, woolly, pale-yellow needles, m p 116–17°. (Found. C, 64 6; H, 4 7; $C_{17}H_{16}O_6$ requires C, 64·5; H, 5·0 per cent)

Ethyl-β-naphtha-furane-9-carboxy-2-carboxylate.—The foregoing compound (1 g) was dissolved in the minimum quantity of absolute alcohol (7 c.c). Freshly cut metallic sodium (1 g) was dissolved in absolute alcohol (25 c c.) and was gradually added to the solution of the ester in small quantities with vigorous shaking. The flask was stoppered lightly and left for one hour at room temperature The solution was filtered and acidified with hydrochloric acid The yellow precipitate obtained crystallized in very shiny yellow, micro-crystals, m p 174–75° (Found C, 67·8; H, 4·5; $C_{16}H_{12}O_5$ requires C, 67 6; H, 4·2 per cent.) It gave effervescence with sodium bicarbonate solution.

10-Carbmethoxy-β-naphtha-α-pyrone.—The formyl ester (1 g.) was heated on a sand-bath with acetic anhydride (20 c.c) and anhydrous sodium acetate (2 g.) for 6 hours. The solid obtained was treated in the usual manner and crystallized from hot dilute alcohol in long golden yellow needles, m.p. 177°. (Found. C, 70 5, H, 3·5; $C_{14}H_{10}O_4$ requires C, 70·8; H, 3·9 per cent.)

Methyl-1-methyl-2-hydroxy-3-naphthoate.—The formyl ester (2 g) dissolved in hot methyl alcohol was gradually added to a mixture of zinc amalgam, prepared from zinc dust (20 g.) according to Robinson and Shah[8] and dilute hydrochloric acid (50 c.c, 1 : 1) at 100°, more alcohol being added whenever necessary to keep the ester in solution After one hour, concentrated hydrochloric acid (10 c.c.) was added and heating continued for a further half hour. The hot liquid was filtered, alcohol evaporated and the

acidic solution extracted with ether. The yellow solid obtained on the evaporation of ether crystallized from very dilute hot alcohol in long, pale yellow needles, m.p 70–71° (Found: C, 71·9; H, 5·5; $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·5 per cent.) It gave blue colouration with alcoholic ferric chloride, did not react with 2·4-dinitro-phenyl hydrazene, did not dissolve in nor gave effervescence with sodium bicarbonate solution

Methyl-1-methyl-2-hydroxy-3-naphthoic acid.—Hydrolysis of the foregoing reduced ester by sodium hydroxide afforded a yellow solid, which on treating with sodium bicarbonate solution and subsequent acidification was finally obtained as a yellow solid which crystallized from hot dilute alcohol in very shiny yellow micro-crystals, m p 235° (Found· C, 71 6; H, 4·9; $C_{13}H_{10}O_3$ requires C, 71·3, H, 4·9 per cent) It sublimed on heating in a dry test-tube, gave effervescence with sodium bicarbonate solution and gave an intense blue colouration with alcoholic ferric chloride

Clemmensen reduction of the formyl ester with glacial acetic acid as solvent.—The formyl ester (0·5 g) was dissolved in glacial acetic acid and added to zinc amalgam prepared from zinc dust (15 g) as usual Concentrated hydrochloric acid (10 c c) was added to it and heated on a water-bath, the mixture being tested for the formyl group every five minutes with 2·4-dinitrophenyl-hydrazine The heating was continued till the solution in the flask gave no precipitate with the hydrazine, which meant the completion of the reduction, and the solution was filtered hot. The filtrate deposited some pasty mass, which was purified and crystallized from hot dilute alcohol in shiny, yellow micro-crystals, m p 235°. This was identified as 1-methyl-2-hydroxy-3-naphthoic acid by the mixed melting point with the previously obtained acid in the last experiment

The zinc amalgam was extracted with ether which on the evaporation gave a pasty mass and some yellow, crystalline solid. These were mechanically separated and the yellow crystals repeatedly crystallized from glacial acetic acid in shiny yellow micro-crystals, m p 223°. (Found. C, 73 6; H, 5·6.) It was insoluble in sodium hydroxide and sodium bicarbonate solutions. It did not give any colouration with alcoholic ferric chloride nor reacted with 2:4-dinitrophenyl hydrazene. The pasty mass on treating as usual with sodium bicarbonate solution and subsequent acidification, afforded 1-methyl-2-hydroxy-3-naphthoic acid, m p 235° which was identified by mixed melting point with the previously obtained acid

The reduction experiment was repeated using glacial acetic acid as solvent, the heating being stopped after one hour.

The hot solution was filtered and deposited some yellow crystals, m.p 250° and a pasty mass which were separated mechanically. The pasty mass on treating with sodium hydroxide solution and subsequent acidification gave 1-methyl-2-hydroxy-3-naphthoic acid, m p. 255°. Mixed melting point with the previously obtained acid was undepressed.

The yellow crystals on repeated crystallization from glacial acetic acid gave yellow micro-crystals, m.p. 263–65° (Found: C, 70 9; H, 5·1 per cent) It dissolved neither in sodium hydroxide nor sodium bicarbonate solutions It did not react with dinitrophenyl-hydrazine nor gave any colouration with alcoholic ferric chloride

In another experiment, the reaction mixture was heated for 4 hours, and on giving the usual treatment, both the filtrate and the zinc amalgam yielded the product melting at 265°

1-formyl-2-hydroxy-3-naphthoic acid.—The formyl ester (0·5 g.) was hydrolysed as usual, with alcoholic sodium hydroxide solution (10%) The solid obtained on acidifying the filtered alkaline solution, was washed and taken through sodium bicarbonate solution (5%) and filtered. On acidifying the filtrate with hydrochloric acid, a yellow solid was obtained which crystallized in shining yellow micro-crystals from hot alcohol, m p. 222–23° Mixed melting point with the previously obtained acid was unaltered. (Found. C, 63·6, H, 4·0, $C_{13}H_8O_4 + \frac{1}{2}H_2O$ requires C, 64 0, H, 4 0 per cent.)

Decarboxylation of the foregoing acid (0 3 g.) by heating it in a sealed carius tube with water (10 c.c.) and hydrochloric acid (1 c.c.) for 6–8 hours at 198–200° afforded a sticky paste This, on triturating with sodium bicarbonate solution and filtration, left an insoluble pasty mass. This was washed with water and crystallized from boiling water in very lustrous, white silvery plates, m.p 124–25°, and identified as β-naphthol.

The repetition of the experiment by heating the carius tube at a lower temperature and for a shorter time resulted in the formation of β-naphthol and some undecarboxylated acid.

Summary

1. Methyl-2-hydroxy-1-formyl-3-naphthoate was synthesised by the action of hexamethylene-tetramine on methyl-2-hydroxy-3-naphthoate.

2. Similar formylation of methyl-2-hydroxy-1-naphthoate was attempted with negative results.

Reference

1. Desai, Radha and Shah . (Under publication).

THE ACTION OF HEXAMETHYLENE TETRAMINE ON PHENOLS AND THE METHYL ESTERS OF PHENOL CARBOXYLIC ACIDS

Part IV. The Synthesis and Study of Methyl-1-hydroxy-4-formyl 2-naphthoate and 2-Acetyl-4-formyl-α-naphthol

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IN continuation of the previous work[1] the formylation of phenols and phenol-carboxylic esters has now been extended to methyl-1-hydroxy-2-naphthoate, 2-acetyl-α-naphthol and 4-acetyl-α-naphthol

Methyl-1-hydroxy-2-naphthoate on formylation with hexamethylene tetramine in glacial acetic acid, yielded a mixture of methyl-1-hydroxy-4-formyl-2-naphthoate and 1-hydroxy-4-formyl-2-naphthoic acid The structure of the latter was established by the hydrolysis of the former The formyl ester and acid both were characterized by their functional derivatives, like 2:4-dinitrophenyl hydrazones and semicarbazones. Clemmensen reduction of the formyl ester afforded methyl-1-hydroxy-4-methyl-naphthoate, which on hydrolysis gave the corresponding acid This acid on decarboxylation yielded the known 4-methyl-α-naphthol of Lesser[2] which proved the 4-position of the formyl group and the structure of the formyl ester

The formyl ester with ethyl aceto-acetate, ethyl malonate and ethyl-bromo-acetate afforded, 3-carbmethoxy-4-hydroxy-naphthylidene ethyl-aceto-acetate, 3-carbmethoxy-4-hydroxy-napthylidene ethyl malonate and ethyl-4-formyl-2-carbmethoxy naphthalene 1-*o*-acetate respectively. On Perkin's acetylation the hydroxyl group got acetylated and methyl-1-acetoxy-4-formyl-2-naphthoate was obtained.

2-acetyl-α-naphthol on similar formylation afforded 2-acetyl-4-formyl-α-naphthol. The formyl ketone did not undergo Knoevenagel condensation with ethyl acetoacetate and ethyl malonate, nor did it condense with ethyl bromo acetate. When subjected to Perkin's acetylation the ketone was recovered and Clemmensen reduction gave an oil which would not solidify.

The formyl ketone was characterized by the preparation of 2:4-dinitro-phenyl-hydrazone and semicarbazone.

4-Acetyl-α-naphthol, could not be similarly formylated and the original ketone was recovered quantitatively.

Experimental

Formylation of methyl-1-hydroxy-2-naphthoate: Methyl-1-hydroxy-4-formyl-2-naphthoate and 1-hydroxy-4-formyl-2-naphthoic acid.—A mixture of methyl-1-hydroxy-2-naphthoate (10 g.), hexamethylene tetramine (30 g.) and glacial acetic acid (50 c c) was refluxed on a water-bath for 5–6 hours and further half an hour more after the addition of dilute hydrochloric acid (50 c c, 1 : 1) The solid that separated was filtered, washed and taken through sodium bicarbonate solution (5 per cent) The insoluble solid was washed with water and was crystallized from hot dilute alcohol in long golden yellow needles, m p 123–24° (Yield, 4 5 g) Recrystallization from glacial acetic acid gave very shiny, yellowish brown plates, m p. 126–27°. (Found. C, 68·4; H, 4 8; $C_{12}H_{10}O_4$ requires C, 67·8, H, 4 4 per cent) It gave a bluish purple colouration with alcoholic ferric chloride

The sodium bicarbonate-soluble portion was obtained by acidifying the filtrate with dilute hydrochloric acid The solid obtained was washed and crystallized from very dilute alcohol in yellow-micro-crystals (0 98 g.) m p 250°. Mixed melting point with 1-hydroxy-4-formyl-2-naphthoic acid (described later) was undepressed. It gave effervescence with sodium bicarbonate solution and reacted with 2. 4-dinitrophenyl hydrazine and semicarbazide

The formylation did not succeed if the methyl ester was replaced by the acid. The reaction gave a complex, yellow, nitrogenous and high-melting compound.

The 2: 4-dinitrophenyl-hydrazone, prepared as usual, crystallized in orange needles from glacial acetic acid, m.p 267–69° (Found: N, 13·4, $C_{19}H_{14}O_7N_4$ requires N, 13·7 per cent)

The 4-nitrophenyl-hydrazone, prepared in the usual manner crystallized in orange-red needles from acetic acid, m p 267–68°. (Found. N, 11·3; $C_{19}H_{16}O_5N_3$ requires N, 11·5 per cent.)

The semicarbazone, prepared as usual, crystallized in shining pale yellow, microcrystals, from alcohol, m.p. 275°. (Found: N, 14 4; $C_{14}H_{16}O_4N_3$ requires N, 14·6 per cent.)

3-Carbmethoxy-4-hydroxy-napthylidene aceto-acetate.—Piperidine (4 drops) was added to a mixture of methyl-1-hydroxy-4-formyl-2-naphthoate (2 g.) and ethyl acetoacetate (2 g.), dissolved in pyridine (10 c.c.). The

mixture was heated on a boiling water-bath for 2 hours. The solid obtained on acidification with hydrochloric acid, was crystallized from hot alcohol in colourless tiny needles, m.p. 133–34°. Mixed melting point with the formyl ester was 95–118°. (Found. C, 66·4; H, 5 3; $C_{18}H_{18}O_6$ requires C, 66·7; H, 5·3 per cent.).

3-Carbmethoxy-4-hydroxy-naphthylidene-ethyl-malonate —Piperidine (3 drops) was added to a mixture of the formyl ester (2 g.) and ethyl malonate (2 g.) dissolved in pyridine (10 c c). The mixture was heated on a water bath for 2 hours and the solid obtained on acidifying it with hydrochloric acid, crystallized from alcohol in colourless tiny needles, m p 142–43° (Found: C, 64 1, H, 5·5, $C_{20}H_{20}O_7$ requires C, 64 5; H, 5 3 per cent)

Ethyl-4-formyl-2-carbmethoxy-naphthalene-1-o-acetate.—To a solution of the formyl ester (1 g) in dry acetone (100 c c), ethyl bromo-acetate (1·5 c c) and anhydrous potassium carbonate (2 g) were added The mixture was well shaken and refluxed on a water-bath for 10 hours The excess of brom-acetic ester and acetone were driven off in a current of air, after filtering off the potassium carbonate The white solid obtained, was crystallized in pale-yellow micro-crystals from hot alcohol, m p 205–06° (Found: C, 64·7; H, 5 5; $C_{17}H_{16}O_6$ requires C, 64·5; H, 5 0 per cent)

Methyl-1-acetoxy-4-formyl-2-naphthoate —The formyl ester (1 g.) was heated with acetic anhydride (10 c c) and anhydrous sodium acetate (1 g) on a sand-bath for 6–7 hours. The solid obtained was worked up as usual and crystallized from dilute hot alcohol in colourless, shiny, micro-crystals, m p. 182–83° (Found C, 59 1, H, 5 2, $C_{15}H_{12}O_5 + H_2O$ requires C, 58·8; H, 5·2 per cent.)

Methyl-1-hydroxy-4-methyl-2-naphthoate.—The formyl ester (2 g), dissolved in hot alcohol, was gradually added to a mixture of zinc amalgam prepared from zinc dust (15 g.), according to Robinson and Shah[8] and dilute hydrochloric acid (50 c.c., 1 : 1) at 100°, more alcohol being added whenever necessary to keep the ester in solution. After 1 hour, concentrated hydrochloric acid (10 c.c.) was added and heating continued for a further half hour. The hot filtrate, on cooling, deposited long, pinkish, shiny micro-crystals, m p 109–10°. (Found: C, 72·3; H, 5·3, $C_{13}H_{12}O_3$ requires C, 12·2; H, 5·5 per cent.)

1-Hydroxy-4-methyl-2-naphthoic acid.—The foregoing reduced ester (0·5 g.) was hydrolysed in alcoholic alkaline solution as usual. The solid obtained on acidification with hydrochloric acid was taken through sodium bicarbonate solution (5%), filtered and again acidified with dilute hydrochloric acid. The

solid obtained crystallized from very dilute alcohol in pinkish micro-crystals, m.p. 209–10°. (Found: C, 71 0; H, 4 8. $C_{12}H_{10}O_3$ requires C, 71·3; H, 4·9 per cent.) *Decarboxylation* of 1-hydroxy-4-methyl-2-naphthoic acid (0·5 g.) by heating with acidulated water (10 c c) in a sealed carius tube for 6–8 hours at 180–90°, gave a black solid This was triturated with sodium bicarbonate solution and the insoluble solid crystallized from boiling water in long, pinkish needles, m p 86–87° This was identified as 4-methyl-α-naphthol by a mixed m p with an authentic specimen.

1-*Hydroxy-4-formyl-2-naphthoic acid* —Methyl-1-hydroxy-4-formyl-2-naphthoate (0·5 g.) was dissolved in sodium hydroxide solution (20 c.c , 10%) and heated on a water bath for 2 hours. The solution was filtered and acidified with hydrochloric acid. The pale yellow solid obtained was washed and crystallized from hot dilute alcohol in pale yellow woolly needles, m.p. 250–52° Mixed melting point with the previously obtained acid was undepressed (Found. C, 66 6, H, 4 1; $C_{12}H_8O_4$ requires C, 66·6; H, 3·7 per cent) It gave effervescence with sodium bicarbonate solution and bluish-purple colouration with alcoholic ferric chloride

Decarboxylation of the foregoing formyl acid (0·5 g.) by heating it with water (10 c.c.) and hydrochloric acid (1 c.c.) in a sealed carius tube 160–80° for 6–8 hours, gave a solid which on treating in the usual way afforded a compound which crystallized in very long, pinkish needles from hot water, m.p. 95–97°, and the mixed melting point with an authentic specimen of α-naphthol was undepressed

Formylation of 2-acetyl-α-naphthol *2-Acetyl-4-formyl-α-naphthol* —A solution of dry 2-acetyl-α-naphthol (10 g), hexamethylene tetramine (30 g) in glacial acetic acid (50 c c.) was first heated on a water-bath for 3–4 hours and then refluxed on a sand-bath for 3 hours and further heated for 3 hours on a water-bath after the addition of hydrochloric acid (100 c.c., 1 : 1).

The solid which separated out in very fine long needles, was filtered, washed and crystallized from glacial acetic acid in long golden yellow needles, m p. 154–55° The acidic filtrate yielded some more of the compound on extraction with ether. Total yield (3·3 g.). (Found: C, 72·6, H, 4·4; $C_{12}H_{10}O_3$ requires C, 72 9; H, 4·6 per cent) The formyl compound was fairly soluble in alkali and with alcoholic ferric chloride, it gave a dark-green colouration. It was very soluble in alcohol, acetone and fairly soluble in acetic acid from which it was crystallized

The 4-nitrophenyl-hydrazone prepared in the usual manner, crystallized from glacial acetic acid in orange-red micro-crystals, m.p. 295° (decomp.). (Found: N, 11·8; $C_{19}H_{14}O_4N_4$ requires N, 12·0 per cent.)

The 2:4-dinitrophenyl hydrozone prepared as usual crystallized in small shiny micro-crystals from acetic acid, m.p. 285° (decomp). (Found: N, 14·1; $C_{19}H_{14}O_8N_4$ requires N, 14 2 per cent.).

The semicarbazone, prepared as usual, gave pale yellow shining micro-crystals from boiling alcohol, m p. 298° (decomp.). (Found· N, 15·3; $C_{16}H_{19}O_3N_5$ requires N, 15·5 per cent)

SUMMARY

Methyl-1-hydroxy-4-formyl-2-naphthoate and 2-acetyl-4-formyl-α-naphthol have been synthesised by the action of hexamethylene tetramine in glacial acetic acid, on methyl-1-hydroxy-2-naphthoate and 2-acetyl-α-naphthol respectively.

Similar formylation of 4-acetyl-α-naphthol did not succeed

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1 Desai, Radha and Shah (Under publication)
2. Lesser, A. 402, 24
3 Robinson and Shah, J 1934, 1497.

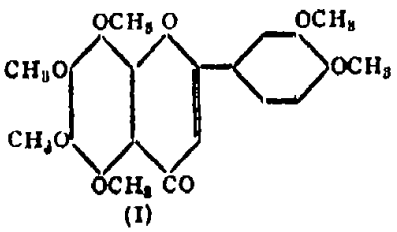
SYNTHESIS AND STUDY OF 5:6:7:8-HYDROXY-FLAVONOLS

By T. R Seshadri and V Venkateswarlu

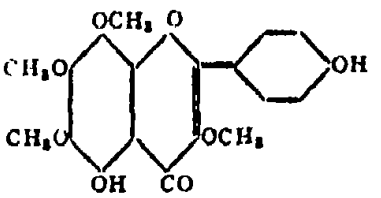
(From the Department of Chemistry, Andhra University)

Received February 5, 1946

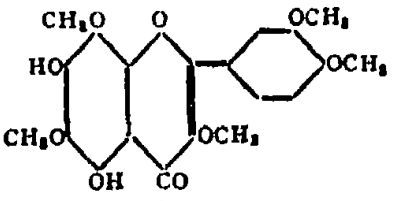
Flavones and flavonols with hydroxyl groups in all the four positions, 5, 6, 7 and 8, seem to be more widely occurring in nature than originally expected. They are, however, recent discoveries and they do not occur free as such, but are found to be partially or completely methylated. Nobiletin (I) is a fully methylated flavone of this type and it was isolated by Tseng[1] from the peels of the Chinese Mandarian oranges (*Citrus nobilis*). Robinson and Tseng[2] established its constitution as 5·6 7:8·3′·4′-hexamethoxy flavone. It has recently been synthesised by Horii[3] by the condensation of 2-hydroxy-3·4:5 6-tetramethoxy-acetophenone with veratroyl chloride and the conversion of the product into the flavone according to the method of Baker and Venkataraman Calycopterin (II) is a partially methylated flavonol, isolated earlier by Ratnagiriswaran, Sehra and Venkataraman[4] from the coppered coloured leaves of *Calycopteris floribunda*. It was also found to be present in the leaves of *Digitatis thapsi* (Spanish digitalis) by Karrer[5] and hence called also by the name thapsin. Its constitution has been recently given as 5.4′-dihydroxy-3.6:7.8-tetramethoxy-flavone (II)[6] Erianthin (III) is also considered to be a flavonol of this series; it is partially methylated and has been recently obtained from the plant, *Blumea eriantha* D.C. by Bose and Dutt[7]



(I)



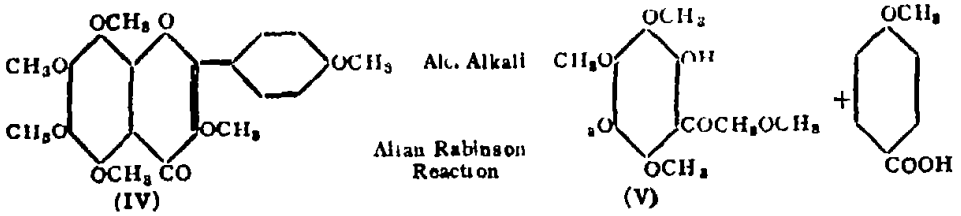
(II)



(III)

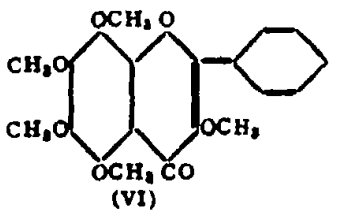
So far these are the only compounds that have been studied in detail. Some other substances isolated in this laboratory seem also to belong to this group. Full information is not available about these compounds enabling the identification of new members easy and this is particularly necessary since frequently these substances could be isolated only in very small quantities A more detailed study of the hexahydroxy-flavone, calycopteretin, has therefore been made now. Further, other members of this flavonol group have also been prepared and their reactions and derivatives studied in detail

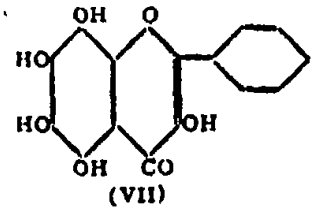
The dimethyl ether of calycopterin is more easily obtained pure by methylating calycopterin with dimethyl sulphate and potassium carbonate in anhydrous acetone solution When subjected to hydrolytic fission with 8% absolute alcoholic potash, it yields, besides anisic acid, a ketonic product as a low melting solid which could also be characterised by the preparation of the 2.4-dinitrophenyl-hydrazone Analytical data of these two substances and reactions show that the ketone is 2-hydroxy-ω: 3:4·5.6-pentamethoxy-aceto-phenone (V) Condensation of the ketone with anisic anhydride and sodium anisate yields dimethyl calycopterin These experiments confirm the results of previous workers[4,5,6] that calycopterin is a tetramethyl ether of 3:5.6:7 8.4'-hexahydroxyflavone

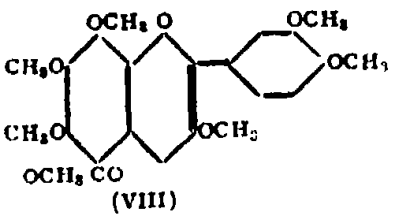


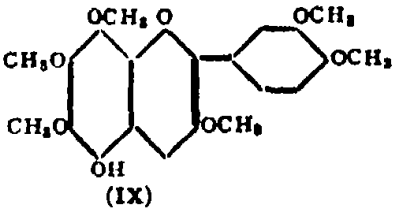
Starting from the above ketone the other members of this flavonol group have been obtained The following is a brief account of the results. The ketone condensed with benzoic anhydride and sodium benzoate smoothly yielding 3:5:6:7:8-pentamethoxyflavone (VI) as the sole product. On demethylation the corresponding penta-hydroxy compound, 6.8-dihydroxy-galangin (VII) was obtained By the condensation of the abovementioned ketone with the anhydride and sodium salt of veratric acid, two products were isolated, one of which separated out from alkaline solution and consisted essentially of the normal hepta-methoxy flavone (VIII) and the other separated from the solution after saturation with carbon-dioxide and consisted mainly of the partially demethylated product (IX) showing the properties of a free hydroxyl in the 5-position. Examination of these revealed that they were still mixtures with indefinite melting points and purification

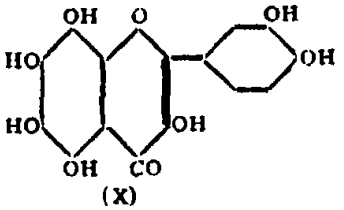
could not be achieved satisfactorily. However by methylating them a pure sample of the hepta-methoxy flavone (VIII) and by demethylating them the corresponding hepta-hydroxy flavone, 6 : 8-dihydroxyquercetin (X) were readily obtained. A pure sample of 5-hydroxy-3 : 6 : 7 : 8 : 3' : 4'-hexa-methoxyflavone (IX) could, however, be obtained by ether-extracting the aqueous mother-liquor after the filtration of the impure sample of (IX) that first separated out. It gave a prominent ferric chloride colour and a sparingly soluble potassium salt when treated with alcoholic potash.


(VI)


(VII)


(VIII)

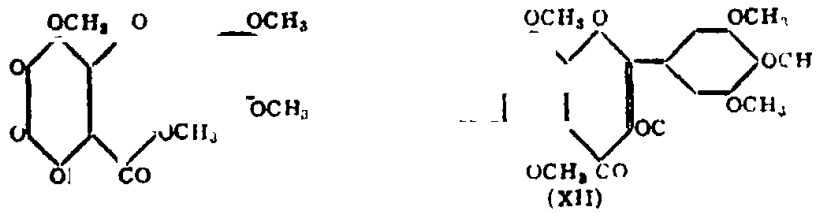

(IX)


(X)

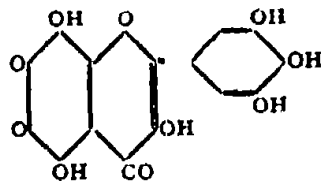
According to Bose and Dutt[7] methyl erianthin should be identical with the abovementioned 5-hydroxy-hexamethoxy flavone (IX) But the recorded properties are not the same. Methyl erianthin is reported to crystallise in the form of needles and melt at 141°. The above hydroxy flavone (IX) crystallises in the form of plates and melts at 122°. The lower melting point of compound (IX) may be considered to be genuine from a comparison of analogous 5-hydroxy-compounds and the related fully methylated flavonols given in Table I. For example, monomethyl calycopterin melts at 124° whereas the dimethyl ether melts at 134°. The 5-hydroxy-compound (XI) described later on also melts 10° lower then the fully methylated ether.

When the anhydride and the sodium salt of trimethyl-gallic acid were used for the above Allan-Robinson condensation the product consisted entirely of the 5-hydroxy compound (XI). The octamethoxy flavone (XII)

was obtained from it by methylation and the octahydroxy compound (XIII), 6 : 8-dihydroxymyricetin by demethylation. This is the most highly hydroxylated compound of the flavone group known so far and is thus of special interest



(XII)



(XIII)

For the purpose of conveniently naming them, the new flavanols are considered to be derived from the series, galangin, kæmferol, quercetin and myricetin which have the 5 7-arrangement of hydroxyl groups and which seem to be more fundamental in evolution giving rise to the others by oxidation of the nuclear positions concerned

The above hydroxyflavonols are in general yellow crystalline substances, the colour changing to green on storage While 6 · 8-dihydroxygalangin is the most stable, retaining its yellow colour for several months, the others change from yellow to greenish yellow and green, the rapidity of the change reaching the maximum with the octa-hydroxy compound, 6 : 8-dihydroxy-myricetin. With water, even in the cold, they give a green colour and on boiling, the colour intensifies to deeper green or blue Even an alcoholic solution changes colour from yellow to green and blue on standing or heating. Crystallisation of the flavonols should not be done with solvents like alcohol and acetic acid and it is best effected by using pure dry ethyl acetate. The pure substances do not exhibit any fluorescence in alcoholic solution or even in concentrated sulphuric acid. Like most hydroxy-flavonols they all give bright red colour when treated with magnesium and hydrochloric acid in alcoholic solution.

The new series of flavonols can be viewed in two ways, (1) as 5 : 7 : 8-hydroxyflavonols with an additional hydroxyl group in the 6-position and (2) as 5 : 6 . 7-hydroxy flavonols with an additional hydroxyl group in the 8-position. In conformity with the first point of view, they exhibit colour

changes in alkaline solutions more remarkable than the members of the gossypetin series These have been studied in detail using buffer solutions and the results may be useful for purposes of identifying samples. But they do not react with *p*-benzoquinone in the manner characteristic of gossypetin and its analogues Bargellini's test yielding green flocks, which is characteristic of the quercetagetin series of flavonols is not given by the new flavonols. Thus the presence of one more hydroxyl group in them causes marked differences in properties

The fully methylated ethers are colourless substances, insoluble in aqueous alkali and giving no colour with alcoholic ferric chloride The ethers which have a free hydroxyl in the 5-position dissolve in aqueous alkali only with difficulty, form sparingly soluble potassium salts with alcoholic potash and give prominent ferric chloride colour

The acetates are also colourless solids Their crystallisation from boiling alcohol seems to bring about partial hydrolysis and the products assume colour on storage It should therefore be carried out using anhydrous solvents or in the cold using acetone-alcohol mixture

Table I gives some of the important data relating to this new series of flavonols and their derivatives

TABLE I

Flavonols	6 : 8-Dihydroxy galangin	Calycopteretin	6 : 8-Dihydroxy quercetin	6 8-Dihydroxy-myricetin
1 Alc $FeCl_3$	Olive green changing to brown	Bright green changing to brown	Deep green changing to brown	Deep green changing to brown
2. Mg+HCl	Orange red	Red	Deep red	Deep red
3. M p of the flavonols	257–58° (with decom)	318–20° (with decomp)	Turns dark above 300, does not melt below 360°	Turns dark above 300°; does not melt below 360°
4. M p. of the acetates	201–03°	218–20°	221° with sintering at 219°	225° with sintering 221°
5. M p. of the fully methylated ethers	80–82°	133–34° 131° (Shah *et al*[6])	129–31°	122–23°
6 M p of partial methyl ethers with the 5-hydroxyl alone free		124° (Shah *et al*[6])	122–23°	113–15°

EXPERIMENTAL

Methylation of calycopterin : Dimethylcalycopterin (IV).—

Calycopterin (1·0 g.) was dissolved in dry acetone (25 c.c.), treated with dimethyl sulphate (1·0 c c.) and anhydrous potassium carbonate (10·0 g)

and boiled under reflux for a period of 20 hours. The solvent was then removed by distillation and the residue treated with water (150 c c.) The methyl ether soon separated out On crystallisation from alcohol, it came out in sheaves of colourless elongated needles melting at 133–34° (*Cf* Shah *et al.*,[6] pale yellow needles, m p. 131°) and did not dissolve in aqueous alkali. (Found: C, 62·9; H, 5·7, OCH_3, 46 0; $C_{21}H_{22}O_8$ requires C, 62·7, H, 5·5, OCH_3, 46 2%) Yield, 1·0 g

Decomposition of the methyl ether with alcoholic potash Isolation of anisic acid and ketone (V) —

Dimethyl calycopterin (1·0 g) was boiled under reflux with 8% absolute alcoholic potash (30 c c) for a period of six hours At the end of this period, as much of the alcohol as possible was removed by distillation and the residue dissolved in water The solution was filtered from any suspended impurities, and then acidified with dilute sulphuric acid The precipitated crystalline solid was filtered, washed with cold water and then crystallised from boiling water when it came out as colourless rectangular plates and prisms melting at 185° It was found to be anisic acid The mixed melting point with an authentic sample of anisic acid was undepressed. The filtrate was repeatedly ether-extracted and the combined ether solution washed with sodium bicarbonate solution (5%) to remove completely the acid part. The ether solution was then washed with water and the solvent evaporated The residue was a pale yellow liquid which solidified on keeping in an ice-chest for a number of days. It crystallised from petroleum ether (b p about 60°) as pale yellow rectangular plates and prisms melting at 65–67° (Karrer[5] gives mp. 66–67°). It gave a green colour with alcoholic ferric chloride. Yield, 0·38 g. (Found: C, 54·8; H, 6 1; OCH_3, 53 9; $C_{13}H_{16}O_7$ requires C, 54 6; H, 6·3; OCH_3, 54 2%) The ketone was also characterised as its 2 : 4-*dinitrophenylhydrazone* in the following manner.

The ketone (0·2 g) dissolved in alcohol (2 c c.) was treated with 2 : 4-dinitrophenylhydrazine (0·2 g) in alcohol (2·0 c.c.). The clear solution was then boiled under reflux on a water-bath for ½ hour. On cooling the alcoholic solution, the phenylhydrazone separated out. In was filtered and crystallised from dilute alcohol when it came out as short orange red rectangular prisms melting at 174–75° (Found · C, 45 2; H, 5 0; OCH_3, 31 1; $C_{19}H_{22}O_{10}N_4$, $2H_2O$ requires C, 45 4; H, 5 2, OCH_3, 30 9%) Loss on drying could not be estimated as the substance sublimed easily above 100° *in vacuo*.

Synthesis of dimethyl calycopterin (IV).—

An intimate mixture of sodium anisate (2 g), anisic anhydride (4·0 g) and the ketone (V) (0·75 g.) was heated in an oil-bath at 180° *in vacuo* for a

period of five hours. The hard mass was then broken up and dissolved in alcohol (50 c.c.). To the solution boiling under reflux was added aqueous potassium hydroxide solution (5 g. in 10 c.c. of water) during the course of half an hour and the boiling continued for another half-hour in order to decompose completely the unreacted anhydride. The alcohol was then removed by distillation under reduced pressure and the residue treated with excess of water The methyl ether separated out as long needle-shaped colourless crystals It was filtered and the product was crystallised from dilute alcohol when it came out as sheaves of colourless elongated needles melting at 133–34°. The mixed melting point with the sample obtained directly from calycopterin by methylation was undepressed Yield, 0·5 g.

The clear alkaline solution from which the hexamethyl ether had separated out was then saturated with carbon dioxide No product was obtained even by ether extraction.

Demethylation of Calycopterin: Calycopteretin (6 : 8-*dihydroxy-kæmpferol*).

Calycopterin (0·5 g) was dissolved in acetic anhydride (10 0 c c.) and treated with hydriodic acid (10 0 c c.; d 1 7) with cooling. The clear solution was then boiled under reflux for half an hour, poured into ice-water and iodine present decomposed by passing sulphur-dioxide gas The precipitated flavonol was twice recrystallised from ethyl acetate when it came out as bright yellow short rectangular plates, melting with decomposition at 318–20°. When crystallised from acetic acid it came in the form of golden yellow needles which soon turned green on exposure to air. (Found. C, 56·8; H, 3·4; $C_{18}H_{16}O_8$ requires C, 56·6, H, 3·2%) It gave a bright green colour with alcoholic ferric chloride which rapidly changed to brown. The flavonol exhibited a series of colours in alkaline solution, the precise variations depending on the conditions of the reaction. Thus with 5% sodium bicarbonate it slowly dissolved to give a yellowish green and then green colour changing to greenish-blue and blue; it faded after 10 minutes to light green with a green precipitate With 5% sodium carbonate the colours were yellow and deep green, quickly becoming blue on shaking; it then faded and became yellowish green within two minutes, brownish yellow and finally brown. With 5% caustic alkali the solution was reddish brown changing to red.

Calycopterin-hexaacetate.—

A small quantity of the flavonol was acetylated using acetic anhydride and a drop of pyridine and boiling for one hour. The product was then crystallised from cold acetone solution enough ethyl alcohol being added just to start the crystallisation. It came out as colourless needles melting at

218–20°. (Found: C, 56 9; H, 4·1; $C_{27}H_{22}O_{14}$ requires C, 56 8; H,

Condensation of the ketone (V) with benzoic anhydride and sodium benzoate; preparation of pentamethoxy flavone (VI).—

An intimate mixture of benzoic anhydride (10 g), sodium benzoate (2 g) and the ketone (0 75 g) was heated at 175–80° for a period of 5 hours. The product melted completely within the first one hour and later solidified The reaction mixture was broken up in alcohol (50 c c) and while boiling under reflux, a solution of potassium hydroxide (15 g in 25 c c) was added during the course of 20 minutes. The solution was boiled for a further 20 minutes to decompose the anhydride The alcohol was then removed under reduced pressure and the residue treated with water A viscous liquid separated out which did not solidify easily Hence, the mixture was ether extracted, and the ether extract washed with water to remove alkali. After distilling off the solvent, the product was purified by dissolving in acetone and adding petroleum ether when coloured impurities separated out The clear solution was then decanted; evaporation of the solvent left a viscous liquid which solidified during the course of 24 hours on keeping in an ice-chest. The product was further purified by crystallisation from dilute methyl alcohol when it came out as colourless rectangular prisms melting at 80–82°. It was insoluble in dilute alkali and did not give any colour with ferric chloride. (Found: C, 64 6; H, 5·3, $-OCH_3$, 41 6; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5 4, $-OCH_3$, 41 7%) Nothing was obtained on saturating the aqueous alkaline solution with carbon dioxide and extracting with ether.

6 : 8-Dihydroxy-galangin (VII) —

The methyl ether (0 5 g) obtained above was demethylated according to the procedure described for calycopterin. The crude product came out as shining yellow needles It was unaffected by water at ordinary temperature but on heating the solution turned green. Two crystallisations from ethyl acetate yielded yellow rectangular plates melting at 257–58° It did not change colour on exposure to air. With alcoholic ferric chloride, it gave an olive green colour changing to brown. On treatment with concentrated sulphuric acid, the crystals turned orange red, later on dissolving to give a yellow solution. It did not exhibit any fluorescence in daylight. (Found: C, 59·3; H, 3·6; $C_{15}H_{10}O_7$ requires C, 59 6, H, 3·3%.) Yield 0·3 g. The flavanol exhibited the following colour changes in alkaline solution. With 5% sodium bicarbonate, the substance dissolved slowly to form a deep blue solution with a violet tinge which started fading after 12 minutes giving a green precipitate; with 5% sodium carbonate, it gave

immediately a blue colour and faded very fast to yellow and then to pale yellow With caustic alkali, it immediately formed a reddish brown solution, on shaking with air it rapidly became yellow, yellowish green and finally yellow.

The flavonol (VII) was acetylated using acetic anhydride and one drop of pyridine The acetate was purified by crystallisation from acetone-ethyl alcohol mixture as described previously when it came out in the form of colourless needles and rectangular plates melting at 201–03°. (Found. C, 58 7, H, 4·0; $C_{25}H_{20}O_{12}$ requires C, 58·6; H, 3 9%)

Condensation of the ketone (V) with veratric anhydride and sodium veratrate —

An intimate mixture of veratric anhydride (4 g) and sodium veratrate (2 g.) and the ketone (0·75 g) was heated *in vacuo* at 175–80° for a period of 5 hours The product melted and formed a reddish-brown liquid which soon solidified. After the reaction was complete, it was broken up in alcohol (50 c.c.) and while boiling under reflux a solution of potassium hydroxide (5 g.) in 10 c.c. was added during the course of 20 minutes The alcohol was then removed under reduced pressure and the residue dissolved in water. The product (A) that separated out was filtered and the clear filtrate was saturated with carbon dioxide when a yellow solid (B) separated out. (A) melted between 108 and 118° and (B) between 115 and 123°. Purification by fractional crystallisation from alcohol could not be effected successfully as the fractions continued to melt indefinitely and hence product (A) was directly used for complete methylation and product (B) for demethylation

5-*Hydroxy-hexamethoxyflavone* (IX) —

The mother-liquor was extracted twice with ether and on evaporating the solvent, a viscous residue was obtained which solidified on cooling. It was crystallised from dilute alcohol when it appeared as yellow rectangular plates melting 122–23° (*cf* methyl crianthin,[7] yellow needles, m.p. 141°). It appeared to be exclusively the 5-hydroxy compound from the sharpness of its melting point It gave a green colour with ferric chloride and formed a sparingly soluble potassium salt in alcoholic potash. Though it did not dissolve easily in cold aqueous potash, it did so on warming and formed a yellow solution (Found· C, 60 5; H, 5·5, OCH_3, 44·7, $C_{21}H_{22}O_9$ requires C, 60·3, H, 5·3; OCH_3, 44·5%) Yield, 90 mg.

3.5.6:7.8.3′ 4′-*Heptamethoxy-flavone* (*VIII*).—

Product (A) obtained from the above condensation was directly methylated using dimethyl sulphate and potassium carbonate in acetone solution. The heptamethoxy flavone was twice crystallised from alcohol when it came

out in the form of colourless rectangular plates, melting at 129–31°. (Found: C, 61·2, H, 5 9; OCH_3, 50·4; $C_{22}H_{24}O_9$ requires C, 61·1; H, 5·6, OCH_3, 50·2%.)

6 : 8-*Dihydroxy-quercetin* (*X*).—

Product (B) (0 5 g.) was demethylated using hydriodic acid (10 c c) in acetic anhydride solution by boiling for half an hour at 140–50° The cooled solution was then poured into water, and iodine removed with sulphur dioxide. The flavonol was obtained as a yellow crystalline (rectangular plates) powder. It was filtered, washed with water and dried. The crystallisation was effected using a large excess of dry ethyl acetate when the compound came out as yellow rectangular plates and flat needles On heating it darkened in colour above 340° and exhibited no other change till 360°. The crystals turned orange-red on treatment with concentrated suphuric acid and then formed a yellow solution which did not exhibit any fluorescence in daylight. The alcoholic solution gave with ferric chloride an intense green colour which changed to brown (Found: C, 53·7, H, 3·1; $C_{15}H_{10}O_9$ requires C, 53-9, H, 3·0%.) With 5% sodium bicarbonate it first gave a yellow solution which rapidly changed to greenish blue and deep blue within ½ minute and then faded to light green with a green precipitate; with 5% sodium carbonate the colours were yellow, emerald green, deep blue, fading and turning green, brownish yellow and finally brown; with 5% caustic alkali it immediately gave reddish brown changing to dark red

The flavonol was acetylated by boiling with acetic anhydride and a drop of pyridine The acetate was crystallised from acetone-ethyl alcohol mixture as previously described when it came out in the form of colourless rectangular plates and prisms melting at 221–22° with sintering at 219° (Found: C, 55·6, H, 4·0; $C_{29}H_{24}O_{16}$ requires C, 55 4; H, 3 8%.)

5-*Hydroxy*-3 : 6 . 7 8 . 3′ · 4′ . 5′-*heptamethoxy-flavone* (*XI*) —

An intimate mixture of trimethyl gallic anhydride (5 0 g.), potassium trimethyl gallate (3 0 g.) and the ketone (V) (0·75 g) was heated *in vacuo* at 175–80° for a period of 5 hours and the product worked up as before. There was no precipitate from the aqueous alkali solution that was first obtained, indicating absence of the fully methylated compound. However after saturation with carbon dioxide a yellow product separated out and it was extracted with ether. On removing the solvent, it came out as a viscous liquid which solidified on keeping in an ice-chest for 3 days. It crystallised from alcohol as bright yellow rectangular plates melting at 113–15° It gave a brownish green colour with alcoholic ferric chloride and formed a

sparingly soluble potassium salt with alcoholic potash indicating the presence of a free hydroxyl in the 5-position. (Found: C, 59·2; H, 5·6; OCH_3, 48 6; $C_{22}H_{24}O_{10}$ requires C, 58 9; H, 5·4, OCH_3, 48·4%.)

3.5.6:7·8:3′:4′·5′-*Octamethoxy-flavone* (*XII*) —

The above methyl ether (XI) (0 2 g) was further methylated in acetone solution using dimethyl sulphate and anhydrous potassium carbonate by boiling for 12 hours The product was obtained as a liquid which solidified on keeping in the ice-chest for a number of days It was crystallised from dilute alcohol when it came out as colourless rectangular plates melting at 122–23°. It did not give any colour with ferric chloride and did not dissolve in dilute alkali or impart any colour to the solution (Found: C, 60·1; H, 5 7, OCH_3, 53 4; $C_{23}H_{28}O_{10}$ requires C, 60 0; H, 5 6; OCH_3, 53·7%)

6:8-*Dihydroxy-myricetin* (*XIII*) —

The above 5-hydroxy-heptamethoxy-flavone (XI) (0·5 g) was demethylated using hydriodic acid as already described On pouring the cooled reaction mixture into ice-water and reducing iodine with sulphur dioxide, the flavonol separated out as a dark green solid. Direct crystallisation from dry ethyl acetate did not remove amorphous impurities completely. It was therefore dissolved in dry acetone and petroleum ether (b.p. 60°) added until some sticky impurity separated out and settled down; the clear solution was then decanted. On slow evaporation of the solvents, the flavonol separated out in a crystalline condition. Final purification was effected by crystallisation from dry ethyl acetate when it appeared as greenish yellow rectangular plates The substance darkened in colour at 340° and did not melt below 360° It gave a deep green colour changing to brown with alcoholic ferric chloride It assumed a green colour rapidly on exposure to moisture (Found: C, 51 2; H, 3 1, $C_{15}H_{10}O_{10}$ requires C, 51 4; H, 2·9%) With 5% sodium bicarbonate, it gave immediately a blue solution turning deeper blue within 10 seconds; this rapidly faded to yellow with a green precipitate. With 5% sodium carbonate the colours were yellow, emerald green, blue, fading immediately to yellowish brown, red, yellowish brown and brown. With 5% caustic alkali it gave immediately a reddish brown solution changing to red

The flavonol (XIII) (50 mg.) was acetylated using acetic anhydride and a drop of pyridine. The acetate was crystallised from acetone-ethyl alcohol mixture as already described when it came out as clusters of colourless rectangular plates melting at 225° with slight sintering at 221°. (Found: C. 54·2; H, 4·0; $C_{31}H_{28}O_{18}$ requires C, 54·2; H, 3·8%.)

Sodium amalgam in absolute alcohol.—

1 6 · 8-*Dihydroxy-galangin.*—The solution turns green and then the colour gradually fades to greenish yellow with no flocks

2. *Calycopteretin.*—The solution becomes green and changes to greenish yellow and then yellowish brown with no flocks.

3. 6 : 8-*Dihydroxy-quercetin* —The solution turns green and immediately changes to brown and slowly precipitates brown flocks, while the solution becomes colourless

4. 6 : 8-*Dihydroxy-myricetin.*—Brown solution, rapidly precipitates brown-pinkflocks, the solution becoming colourless.

Gossypetone reaction —

1. 6 : 8-*Dihydroxy-galangin.*—The solution immediately becomes blue and rapidly changes to red; this fades on shaking to give a yellow solution changing finally to brown. After 24 hours it is coloured brown.

2 *Calycopteretin* —The blue solution formed immediately changes to deep red and then to green, greenish yellow, brown and yellow. After 24 hours, it is yellow.

3. 6 : 8-*Dihydroxy-quercetin.*—The blue solution immediately changes to brown red and fades to pale yellow. Pale yellow after 24 hours

4. 6 : 8-*Dihydroxy-myricetin.*—The alcoholic solution which was originally green changes to blue and turns into a stable intense red It fades to brown during 24 hours.

Colour reactions with alkaline buffer solutions —

1 6 . 8-*Dihydroxy-galangin.*—

pH 8·0 Substance sparingly soluble, pale yellow solution changing to dirty green, blue, and deep violet blue fading within three minutes and becoming pale blue within six minutes. The pale blue slowly changes and becomes pale yellow within 24 hours

pH 8·6 Substance difficultly soluble, pale yellow solution changing to blue and then to violet blue and fading within two minutes The pale blue slowly fades and finally after 24 hours it becomes pale yellow.

pH 9·2 Substance more easily soluble than before; yellow solution changes to blue and fades faster within the first minute and

becomes yellow by four minutes. After 24 hours it becomes pale yellow.

pH 9·8 Substance dissolves quicker to a yellow solution and becomes blue, starts fading within 20 seconds and becomes pale blue in two minutes and yellow in four minutes After 24 hours it becomes pale yellow

pH 10 4 Pale yellow solution, changes very fast to blue and becomes pale yellow whithin 15 seconds After 24 hours there is no change

pH 11·0 Yellow solution quickly becoming yellowish green, pale blue and finally yellow. After 24 hours it is pale yellow.

pH 11 6 Yellow solution changing fast to yellowish green and greenish blue, becomes yellow within 30 seconds and then golden yellow. Slowly it fades to pale yellow within 24 hours

pH 12 2 Same as above.

pH 12·8 Same as above.

pH 13 4 Same as above.

In general, the flavonol does not dissolve in the buffer solutions of lower pH readily. On boiling with distilled water, the substance forms a green solution which rapidly turns blue. With tap water the solution turns deeper blue than with distilled water and slowly fades and after 24 hours becomes pale yellow

Calycopteretin.—

pH 8·0 Yellow solution, quickly changes to dirty green and to deep blue within half minute, more intense blue within one minute and starts fading within 3 minutes to bluish green. This slowly fades within 10 minutes to yellowish green and becomes pale yellow within 18 minutes. After 24 hours the solution becomes pale yellow.

pH 8·6 Yellow solution slowly changing to yellowish green, and blue in 20 seconds; starts fading after one minute and becomes greenish yellow within 8 minutes. After 24 hours it is pale yellow.

pH 9·2 The initial yellow solution quickly changes to green, blue and intense blue within half minute and fades rapidly to yellow in two minutes. Within six minutes the yellow intensifies and becomes golden yellow. After 24 hours it is pale yellow.

pH 9·8 Colour changes are very rapid; yellow solution turns quickly deep green and within half minute greenish yellow, becomes golden yellow within one minute and orange yellow within two minutes. The solution assumes a yellow colour after 24 hours

pH 10 4 Yellow solution rapidly changes to green, and emerald green and becomes yellowish green within half minute and orange yellow within 45 seconds. The colour fades and becomes golden yellow after 24 hours

pH 11 0 Same as above.

pH 11 6 Yellow solution; colour changes same as above and faster.

pH 12·2 Same as above Changes faster than before giving orange yellow within 20 seconds and deeper yellow after 24 hours

pH 12 8 Same as above.

pH 13·4 Yellow solution becomes greenish yellow and then fades to orange yellow After 24 hours it becomes a deep yellow solution.

With distilled water, the substance becomes green changing to greenish blue The solution is also of the same colour and changes to pure blue on boiling.

6 : 8-*Dihydroxy-quercetin.*—

pH 8 0 Yellow solution becoming deep yellow, turns rapidly yellowish green, green, and emerald green and within 30 seconds turns blue and intensifies to deeper blue in 6 minutes. The blue fades slowly and turns to deep yellow in 24 hours.

pH 8 6 Yellow solution going into deep green within 20 seconds; becomes blue within ½ minute and intensifies to deep blue within one minute and fades after 3 minutes. Becomes pale yellow in 24 hours

pH 9·2 Yellow solution, quickly changes to green and blue within 20 seconds, starts fading within 2 minutes and becomes yellowish green after 6 minutes and yellow after 10 minutes, and pale orange after ½ an hour. Pale yellow solution after 24 hours.

pH 9·8 Yellow solution, changes very fast to greenish yellow and then blue, fades within 30 seconds and becomes greenish

yellow within one minute and yellow in 3 minutes. In 10 minutes becomes orange yellow which fades slowly and becomes yellow in 24 hours.

pH 10·4 Very fast changes; yellow solution immediately turns green and emerald green and becomes greenish yellow and yellow within 20 seconds It assumes a golden yellow colour within one minute and orange within 2 minutes; subsequently fades to paler orange within half an hour; yellow in 24 hours

pH 11 0 Same as above; within one minute deeper orange than above and fades within half an hour to pale orange; solution deep yellow after 24 hours.

pH 11 6 Same as above; assumes orange with ½ minute and orange red within one minute, fades after 30 minutes and becomes deep yellow in 24 hours

pH 12·2 Same as above; deep orange red within 45 seconds and starts fading to become deeper yellow in 24 hours

pH 12·8 Same as above; within 30 seconds deeper orange red; fades after one hour to give deep yellow in 24 hours

pH 13 4 Same as above Solution deeper yellow after 24 hours.

Substance treated with distilled water gives a blue colour in the cold; the colour of the solution changes to green after boiling, fades after ½ hour and becomes pale yellow after 24 hours.

6 : 8-*Dihydroxy-myricetin* —

pH 8 0 Yellow solution changes to yellowish green, green and emerald green and becomes deep blue within one minute; after 10 minutes becomes emerald green and fades after one hour. Deep yellowish brown after 24 hours.

pH 8·6 Yellow solution changes to greenish yellow and then rapidly to green and blue within ½ minute. Fades after 3 minutes to green and becomes pale yellowish green after 6 minutes; in one hour becomes pale yellow; yellow in 24 hours.

pH 9·2 Yellow solution, changing fast to green and then blue within 20 seconds; starts fading after 1½ minutes; yellowish green within 4 minutes and pale yellow in 24 hours.

pH 9·8 Yellow solution rapidly changing to green and emerald green; fades to green within 20 seconds and yellowish green in 2 minutes; brownish yellow in 24 hours.

pH 10·4 Yellow solution changing to green and emerald green and fading to yellowish brown within 40 seconds; colour turns brown within one minute, changes to brown red and reddish purple and fades to reddish brown after 2 minutes, becomes brown within 5 minutes and orange brown within 10 minutes. After 24 hours it is orange red

pH 11 0 Yellow solution changing fast to yellowish green and to reddish purple within one minute and then brilliant purple; slowly fades to reddish brown in 12 minutes and orange red in 24 hours.

pH 11·6 Very rapid changes, initial yellow solution changes to yellowish green, yellowish brown and brown purple within 20 seconds and then to bluish purple; fades after one minute rapidly to reddish brown and becomes yellowish brown after 4 minutes; after 24 hours orange red.

pH 12 2 Faster changes, same as above

pH 12·8 Yellow solution changing fast to green, emerald green and yellowish brown within 20 seconds, becomes brown and brown purple and bluish purple and fades to reddish brown in one minute and pale brown in 6 minutes; after 24 hours orange red.

pH 13·4 Same as above.

On treatment with distilled water the substance turns blue in the cold The solution becomes deeper blue on warming and fades to pale green after 1½ hours. It is greenish yellow after 24 hours

Our thanks are due to Mr. A. N Ratnagiriswaran for the gift of several grams of calycopterin.

SUMMARY

The constitution of calycopteretin has been confirmed by the decomposition of the fully methylated ether with alcoholic alkali and also by its synthesis from the decomposition products. Alkaline hydrolysis of the fully methylated ether yields anisic acid and 2-hydroxy-ω-3 : 4 : 5 : 6-pentamethoxyacetophenone. Condensation of this ketone with sodium anisate and anisic anhydride, regenerates calycopterin dimethyl ether. When the anhydride

and sodium salt of benzoic acid are used instead, 3:5:6:7: 8-pentamethoxy flavone is readily formed On demethylation, it yields 6:8-dihydroxy-galangin When, however, the sodium salt and anhydride of veratric acid are used, partial demethylation takes place in the 5-position, giving rise to both hexamethyl and heptamethyl ethers By complete demethylation, 6:8-dihydroxy-quercetin is obtained Using gallic acid derivatives for the condensation, demethylation is found to be complete in the 5-position yielding 5-hydroxy-heptamethoxy-flavone. Methylation of this produces the octamethyl ether and demethylation the octahydroxy compound, 6:8-dihydroxy-myricetin This is the most highly hydroxylated of flavones known so far

A comparative study of the properties of the four flavonols of this group, their methyl ethers and acetates has been made. Colour reactions useful for rapid identification are also described. They are remarkable in several respects.

The properties of mono-methyl erianthin do not agree with those of 5-hydroxyhexamethoxy-flavone prepared in the course of this work.

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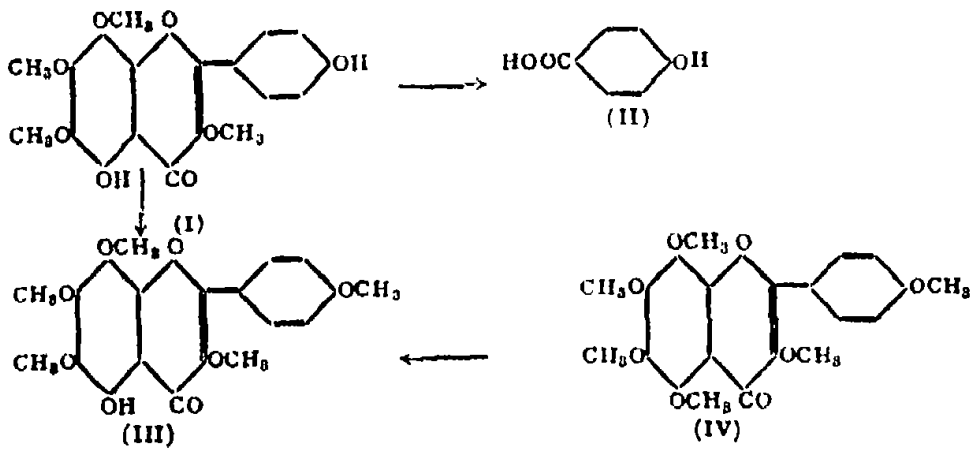
CONSTITUTION OF CALYCOPTERIN

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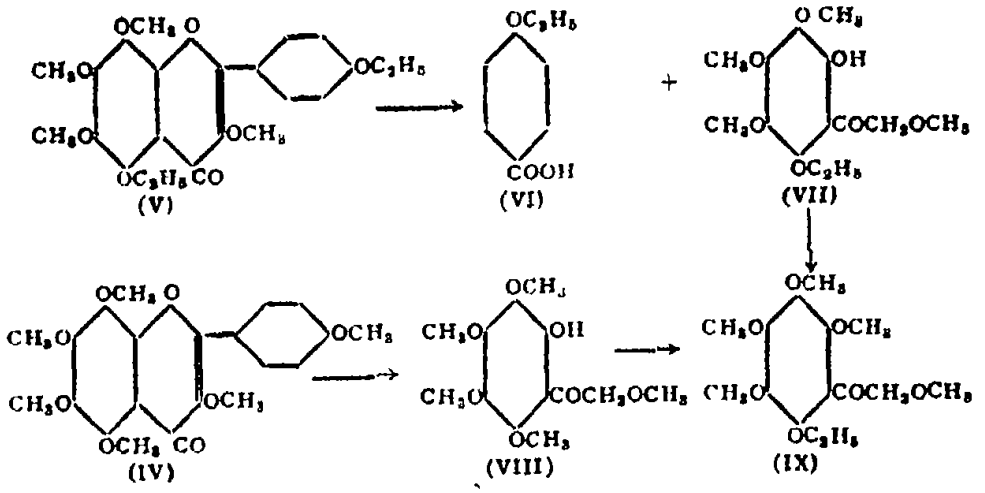
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CALYCOPTERIN is a tetramethyl ether of calycopteretin which is 3 5 6 7 8 : 4'-hexahydroxy-flavone Its exact constitution was first investigated by Gulati and Venkataraman[1] and their conclusions were later modified by Shah, Venkataraman and Virkar.[2] Of the two free hydroxyl groups, one was easily located in the 4'-position by identifying *p*-hydroxybenzoic acid (II) as a product of alkaline fission The position of the other hydroxyl has been finally fixed as 5, since this group is resistant to methylation and the monomethyl ether of calycopterin (III) gives reactions characteristic of a 5-hydroxyl Further this monomethyl ether has been obtained by the partial demethylation of the dimethyl ether (IV) by means of hydrobromic acid Consequently calycopterin is considered to be 5.4'-dihydroxy-3.6:7.8-tetramethoxy-flavone (I)



The above constitution has now been confirmed in a different way Calycopterin is ethylated by means of ethyl iodide and potassium carbonate in acetone solution and the diethyl ether (V) obtained in good yield. When subjected to fission with alcoholic potash, it yields an acid product which is identified as *p*-ethoxybenzoic acid (VI) locating an ethoxyl in the 4'-position of the flavone. The other part is a ketone having the composition and the characteristic properties of 2-hydroxy-monoethoxy-tetramethoxy-acetophenone (VII) In order to determine its constitution it is further methylated by means of dimethyl sulphate and anhydrous potassium carbonate

in acetone solution. This product is found to be identical with the ethylation product (IX) of 2-hydroxy-ω: 3: 4: 5: 6-pentamethoxyacetophenone (VIII). The identity has been established not only by direct comparison but also by the preparation of derivatives. This is possible only if in calycopterin, a free hydroxyl exists in the 5-position which is substituted by an ethoxyl in the ethyl ether The various transformations described above are diagrammatically represented below:



Experimental

Ethylation of calycopterin·—Diethyl-calycopterin (V) —

Calycopterin (1 g) dissolved in acetone (20 c.c.) was boiled under reflux with excess of ethyl iodide (3·0 c c.) and anhydrous potassium carbonate (10 g.) for a period of 15 hours The solution which was originally orange red became practically colourless towards the end. The solvent was then removed by distillation, and the residue treated with ice-water. The ethyl ether which separated out as a liquid solidified during the course of half an hour. When it was crystallised from alcohol it came out as colourless rhombohedral prisms melting at 131–32° (Karrer[3], mp 130°) It was insoluble in dilute alkali and did not give any colour with alcoholic ferric chloride. The mixed melting point with dimethyl-calycopterin was depressed, 105–115°. (Found: C, 64 1, H, 6 1; $C_{22}H_{26}O_8$ requires C, 64 0; H, 6·0%.) It was easily soluble in acetone, ethyl acetate and hot alcohol and very sparingly soluble in cold alcohol

Decomposition of diethyl calycopterin with alcoholic potash.—

Diethyl-calycopetrin (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c., 8%) for a period of six hours. At the end of the

operation, as much of the alcohol as possible was removed by distillation and the residue dissolved in water The solution was then filtered from any suspended insoluble impurities and the clear filtrate was acidified with dilute sulphuric acid. It was then ether-extracted several times and the combined ether extract was shaken three times with 5% sodium bicarbonate solution to remove the acid part (A).

The ketonic part.—The ether solution was then washed with water and on distilling off ether it gave a pale yellow liquid which solidified during the course of a few hours. It was purified by crystallisation from light petroleum (B.P. 60°) when it came out in the form of pale yellow thin rectangular plates melting at 75–77° (Karrer[3] gives mp. 63–64°). It dissolved in alkali to give a yellow solution and gave an olive-green colour with alcoholic ferric chloride. It is highly soluble in water even in the cold (Found: C, 55·9; H, 6 6; $C_{14}H_{20}O_7$ requires C, 56 0, H, 6·7%)

The acid part.—The bicarbonate solution (A) on acidification with concentrated hydrochloric acid precipitated a crystalline material which was ether extracted. The residue obtained after removal of ether was purified by crystallisation from hot water or 10% alcohol when it came out in the form of colourless shining needles melting at 197–98° The mixed melting point with a synthetic sample of *p*-ethoxy-benzoic acid (see below) was undepressed. (Found. C, 65 2, H, 6 2, OC_2H_5, 26 9, $C_9H_{10}O_3$ requires C, 65·1; H, 6·0; OC_2H_5, 27·1%)

p-Hydroxy-benzoic acid (1 0 g.) was ethylated in acetone solution with ethyl iodide (3·0 c.c.) and anhydrous potassium carbonate by boiling for a period of 15 hours. The solvent was removed by distillation and the residue treated with water. The ether-ester that separated out as a liquid was twice extracted with ether On removing the solvent it was again obtained as a liquid. It was then hydrolysed by boiling with 20% sodium hydroxide solution (20 c.c.) for half an hour and the acid obtained on acidification, was crystallised from 10% alcohol when it came out as colourless shining needles melting at 197–98°. Yield 0·9 g

The aqueous potassium carbonate solution from which the ether had separated was acidified with dilute sulphuric acid when a crystalline precipitate separated out. It was crystallised from 10% alcohol and was found to be *p*-ethoxy-benzoic acid. Yield 0·1 g. Thus in the process of ethylation of *p*-hydroxy-benzoic acid some acid is formed along with the ester.

ω: 2: 3: 4: 5-*pentamethoxy-6-ethoxy-acetophenone* (*IX*).—

The above ketone was methylated in acetone solution by boiling with dimethyl sulphate and anhydrous potassium carbonate for a period of ten

hours. The solvent was then removed by distillation, and the residue treated with water when an insoluble liquid separated out and it was extracted with ether. Removal of the solvent gave the methyl ether as a viscous liquid. It did not solidify on keeping in the ice-chest for a number of days and attempts at crystallisation were not successful. It was insoluble in aqueous alkali and did not give any colour with alcoholic ferric chloride. Hence it was considered to be the required ketone and was further identified as its 2:4-dinitrophenyl-hydrazone. This was prepared by boiling the ketone with an alcoholic solution of denitro-phenyl-hydrazine and was obtained as deep red rhombohedral prisms by crystallisation from alcohol or acetic acid melting at 198–99° (Found. C, 57·7, H, 5 9, $C_{21}H_{26}O_{10}N_4$ requires C, 57 5; H, 5 9%.) A mixed melting point with 2:4-dinitro-phenyl-hydrazine was depressed

Ethylation of 2-hydroxy-ω 3 4 5:6-pentamethoxy-acetophenone (VIII) — ω:2·3 4 5-pentamethoxy-6-ethoxy-acetophenone (IX) —

2-Hydroxy-ω 3 4·5 6-pentamethoxy-acetophenone[4] was ethylated in acetone solution by boiling with ethyl iodide and potassium carbonate. The product on working up came as a liquid which could not be solidified. It was insoluble in dilute aqueous alkali and did not give any colour with alcoholic ferric chloride It was identified as its 2: 4-dinitrophenylhydrazone This was prepared as before and it crystallised from acetic acid as deep red rhombohedral prisms melting at 198–99° A mixed melting point with the sample obtained previously was undepressed

Summary

The constitution of calycopterin as 5.4′-dihydroxy-3:6:7.8-tetramethoxy-flavone has been confirmed Calycopterin diethyl ether has been shown to have ethoxyl groups in the 5 and 4′-positions, since on fission with alcoholic alkali, it yields *p*-ethoxy benzoic acid and 2-hydroxy-ω:3:4:5-tetramethoxy-6-ethoxy acetophenone. The constitution of the ketone has been established by methylation and comparison with a synthetic sample obtained by the ethylation of ω 2.3.4:5-pentamethoxy-6-hydroxy-acetophenone

References

1. Gulati and Venkataraman — *J C S*, 1936, 267.
2. Shah, Virkar and Venkataraman — *J. I C S*, 1942, **19**, 135.
3. Karrer, W — *Helv*, 1934, 17, 1560
4. Seshadri and Venkateswarlu — *Proc Ind Acad Sci*, A 1946, **23**, see previous paper.

A NOTE ON THE CONSTITUTION OF ALPINETIN

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FROM the ether extract of the seeds of *Alpinea chinesis*, Kimura[1] isolated alpinetin having a melting point of 223°. Based on a study of its properties and reactions, he considered it to be 5-hydroxy-7-methoxy-flavanone. A substance of this constitution had already been prepared synthetically by Shinoda and Sato[2] and its melting point recorded as 101°. They made it by the partial methylation of 5 7-dihydroxy-flavanone using diazomethane. In view of this discrepancy, 5-hydroxy-7-methoxy flavanone has now been prepared in a different way by the partial demethylation of 5 : 7-dimethoxy flavanone using aluminium chloride in nitrobenzene solution. In its properties it agrees with the description of Shinoda and Sato and it melts at 101–02°. Alpinetin cannot, therefore, be identical with this flavanone and its constitution should be considered as unsettled.

EXPERIMENTAL

5 : 7-Dimethoxy-flavanone —

4 : 6-Dimethoxy-2-hydroxy-acetophenone required for the present purpose was prepared by the partial methylation of phloracetophenone as described by Sastri and Seshadri.[3] It melted at 88–89° and gave a reddish brown colour with ferric chloride.

In the conversion of this ketone into 4 : 6-dimethoxy-2-hydroxy-chalkone[4] the yields and the quality of the product could be improved by adopting the following procedure.

A mixture of 4 : 6 dimethoxy-2-hydroxy-acetophenone (3 g.) and benzaldehyde (9 c.c.) was dissolved in alcohol (20 c.c.) and treated with a strong solution of potash (25 g. of potash in 20 c.c. of water) while cooling in ice. Enough alcohol was then added to get a homogeneous solution and the flask tightly stoppered and left for 3 days at the room temperature. The contents were then diluted with water, extracted twice with ether (A) and the clear alkaline layer acidified with concentrated hydrochloric acid. The product was extracted with ether and the ether solution washed well with aqueous sodium bicarbonate. On distilling off the ether the chalkone was obtained as a red liquid which soon solidified. Yield, 4.0 g.; m.p. 90–91°.

When the ether extract (A) was evaporated, it left a reddish brown oily residue. It was treated with excess of petroleum ether and the mixture kept in the ice-chest. A pale yellow crystalline solid separated out. It was filtered, washed with small quantities of ether and crystallized from a mixture

of benzene and petroleum ether from which it separated in the form of colourless rectangular plates and prisms melting at 143–44°. It was identical with the flavanone described below (Kostanecki and Tambor recorded the melting point of 5:7-dimethoxy flavanone as 1.

For the conversion of the chalkone into the flavanone the former was refluxed with aqueous alcoholic sulphuric acid for 24 hours. The product was ground well with aqueous alkali to remove unchanged chalkone, washed with a little ether to remove coloured impurities and finally crystallised from benzene-petroleum ether mixture. The flavanone separated out as colourless rectangular plates and prisms melting at 143–44°. It was insoluble in aqueous alkali and did not give any colour with ferric chloride. In concentrated nitric acid it dissolved to produce an intense blue colour. When reduced with magnesium and hydrochloric acid in an alcoholic solution, it gave an orange yellow colour

5-Hydroxy-7-methoxy-flavanone.—

A solution of 5:7-dimethoxy-flavanone (0·5 g.) in dry nitrobenzene was treated with a solution of anhydrous aluminium chloride (1 g.) in the same solvent. After keeping the solution at 100° for 1 hour, it was cooled and treated with excess of petroleum ether, whereby most of the nitrobenzene was dissolved, leaving behind a greenish semi-solid mass. It was washed twice with petroleum ether and finally decomposed with dilute hydrochloric acid. The solution along with the solid product was extracted with ether and the ether solution repeatedly shaken with dilute sodium hydroxide solution. A bulky precipitate separated at this stage in the aqueous medium but this dissolved on adding more of water. The alkaline solution was filtered and acidified with hydrochloric acid. The precipitated solid was filtered, washed with water and crystallised successively from alcohol and a mixture of benzene and petroleum ether. 5-Hydroxy-7-methoxy-flavanone crystallised in the form of stout prismatic needles melting at 101–02°. (Found: C, 71·1; H, 5·4; CH_3O, 11·0; $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2 and CH_3O, 11·5%.)

It was sparingly soluble in cold aqueous alkali. In alcoholic solution it gave a deep brown colouration with ferric chloride and an orange colour with magnesium and hydrochloric acid. In concentrated nitric acid it dissolved to a fine blue solution.

References

1. Kimura — *Chemical Abstracts*, 1940, 4063.
2. Shinoda and Sato — *Ibid.*, 1929, 837.
3. Sastri and Seshadri — *Proc. Ind. Acad. Sci.*, A, 1946, 23 (see next issue of the *Proceedings*).
4. Kostanecki and Tambor — *Ber.*, 1899, 2260.

ARYL ESTERS AND ARYLAMIDES OF 2-HYDROXY-3-NAPHTHOIC ACID AND 1-BROMO-2-HYDROXY-3-NAPHTHOIC ACID

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(Communicated by Prof. R. C Shah, F.A.Sc.)

The aryl esters of the acids are prepared by heating the respective phenol and the acid in presence of phosphorus oxy-chloride at 130–140° C. The esters of the bromo acid and *o*-anisidide and *o*-toluidide of the bromo acid are also obtained by the bromination of the esters and the corresponding arylamides of the simple hydroxy acid.

The method for the preparation of arylamides of 2-hydroxy-3-naphthoic acid are either covered by patents or are very tedious,[1] probably because the preparation of its acid chloride is very tedious.[2] Now it is found that these arylamides can be easily prepared by heating the mixture of the acid and the amine with excess of phosphorus trichloride.

In the case of 1-bromo-2-hydroxy-3-naphthoic acid, however, as the acid chloride can be easily prepared by the action of phosphorus pentachloride on the acid in presence of dry benzene, its arylamides are prepared by the interaction of the acid chloride and the respective amine in presence of dry benzene at room temperature.

Experimental

Preparation of aryl esters.—

The acid and the phenol were taken in equal weights and phosphorus oxychloride whose volume was equal to half the weight of the acid was added to the mixture. The mixture was heated at 130–40°, until a clear solution was obtained When cold, the reaction mixture was diluted with water and separated solid was washed completely. All the substances are crystallised from acetic acid. They are described in Table I.

2-Hydroxy-3-naphth-o-toluidide.—A mixture of the acid (4 g.) and freshly distilled *o*-toluidine (5 g.) was heated to melt the acid and then phosphorus trichloride (10 c.c.) was added through the top of the condenser and the mixture was heated at 160–70° for two hours. When cold, the mixture was titurated with dilute hydrochloric acid and washed with water. It

TABLE I

Substance	Crystalline shape	M.P.	Formula	Found	Required	Yield %
o-Cresyl-2 hydroxy-3-naphthoate	Yellow needles	119–20°	$C_{18}H_{14}O_3$	C, 77·4, H 5·0,	C, 77·7 H, 5·0	85
m-Cresyl-2 hydroxy 3-naphthoate	Pale yellow needles	94–5°	$C_{18}H_{14}O_3$	C, 77 7, H, 4·4;	C, 77 7 H, 5·0	80
*Phenyl-1-bromo 2-hydroxy 3-naphthoate	Pale yellow needles	131–2°	$C_{17}H_{11}O_3$ Br.	Br, 23·0,	Br, 23·3	75
*o-Cresyl 1 bromo-2 hydroxy 3-naphthoate	Yellow needles	163–4°	$C_{18}H_{13}O_3$ Br	Br, 22 4;	Br, 22·4	75
*m-Cresyl 1 bromo-2-hyuroxy 3 naphthoate	Pale yellow needles	146–7°	$C_{18}H_{13}O_3$ Br	Br, 22 7,	Br, 22 4	75

crystallised from acetic acid in small white needles, m.p. 192–3°. Yield 35% (D R P 293,897 gave m.p. 195–6°) (Found. N, 4·8; $C_{18}H_{13}O_3N$ requires N, 5·1 per cent)

2-Hydroxy-3-napth-m-toluidide —A mixture of the acid (5 g), *m*-toluidine (6 g.) and phosphorus trichloride (20 c c) was heated under reflux at 170–80° for two hours and then worked up as above It crystallised from acetic acid in shining plates, m p 213–14°. Yield 80% Found: N, 4 9; $C_{18}H_{15}O_2N$ requires N, 5·1 per cent)

2-Hydroxy-3-naphth-o-anisidide —A mixture of the acid (5 g), *o*-anisidine (7 g) and phosphorus trichloride (20 c c) was heated under reflux at 170-90° for two and a half hours and then worked up as before. It crystallised from acetic acid in small needles, m.p 162–4°. Yield 20% (D R P. 293, 897 gave m.p. 167–8°) (Found: N, 4·5, $C_{18}H_{15}O_3N$ requires N, 4·8 per cent)

1-Bromo-2-hydroxy-3-naphthoyl chloride —A mixture of the acid (3 g.) and phosphorus pentachloride (3 g) and dry benzene (10 c.c.) was heated gently on a water-bath until a clear orange solution was obtained. On cooling the solution, yellow needles of the acid chloride separated out. The solid was washed with dry petroleum ether and dried in vacuum over phosphorus pentoxide, m.p. 145–6°. (Found, Cl, 12·2, Br, 27·6; $C_{11}H_5O_2ClBr$ requires Cl, 12 4; Br, 28·0 per cent.)

Arylamides of 1-bromo-2-hydroxy-3-naphthoic acid.—The acid chloride prepared from a certain weight of the acid was dissolved in sufficient quantity of dry benzene (10 times in vol. of the weight taken) and to it the amine, whose volume was equal to the weight of the acid taken, dissolved in a little dry benzene was added and the mixture was left at room temperature for one hour. The solid obtained after the removal of the solvent was treated with dilute hydrochloric acid, washed with water and then crystallised from acetic

The substances are described in Table II.

TABLE II

Substance	Crystalline shape	M.P.	Formula	Found	Required	Yield %
1 Bromo-2hydroxy 3-naphth anilide	Pale yellow needles	165–6°	$C_{17}H_{12}O_2NBr$	Br, 23·1	Br, 23·4	60
*1 Bromo-2 hydroxy 3-naphtha *o*-toluidide	Yellow needles	234–5°	$C_{18}H_{14}O_2NBr$	Br, 22 3	Br 22 5	56
1 Bromo-2 hydroxy 3 naphth *m* toluidide	Yellow plates	171–2°	$C_{18}H_{14}O_2NBr$	Br, 22 9	Br, 22 5	75
1 Bromo 2 hydroxy 3 naphth *p* toluidide	Pale yellow needles	201–2°	$C_{18}H_{14}O_2NBr$	Br, 22·6	Br, 22 5	70
*1-1 romo 2 hydroxy-3 naphth *o*-anisidide	Yellow needles	191–2°	$C_{18}H_{14}O_2NBr$	Br, 21·9	Br, 21 5	60
1-Bromo-2 hydroxy 3 naphth-*p*-anisidide	Yellow plates	173–4°	$C_{18}H_{14}O_2NBr$	Br, 21·2	Br, 21 5	60

Substances marke l * are prepared by direct condensation as well as by the bromination of the corresponding derivatives of the 2 hydroxy-3 napthoic acid

(The preparation of *o*- and *m* cresyl esters of 2 hydroxy-3-napthoic acid and *o*- and *m*-toluidides and *o*-anisidide of the same acid as well as phenyl *o*- and *m* cresyl esters and anilide, *o*-, *m* and *p*-toluidides and *o*- and *p*-anisidides of 1 bromo-2-hydroxy-3 naphthoic acid is described. The esters and *o*-toluidide and *o*-anisidide of 1 bromo-2-hydroxy-3-napthoic acid are also prepared by the bromination of the corresponding derivatives of the 2 hydroxy 3-naphthoic acid)

Bromination of the phenyl, o-, *and* m-*cresyl esters and* o-*toluidide and* o-*anisidide*

The requisite ester (2 g) was mixed with dry chloroform (10 c c) and the solution of bromine in the same solvent (14 c.c. of 10% solution) was gradually added to it. The reaction mixture was left at room temperature for half an hour and then the solvent was removed. The bromo-derivative was crystallised from acetic acid and mixed melting point with the authentic specimen described in Table I was taken, when no lowering in melting point was observed.

In the bromination of *o*-toluidide and *o*-anisidide the same method was used, but they being less soluble, more solvent was used, the proportion of the reactants being 1 : 1. These products also were crystallised from acetic acid and mixed melting points with authentic specimens described in Table II showed no

1. Schoff *Ber*, 1892, 25, 2743, Brit patent 289037, U S patent 1,733, 4(
patent 95038 of 1932, D R. P. 289027, 293897, 294799 of 1916.
M. 1901, 22, 791.
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STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXVII. The Rotatory Dispersion of Stereoisomeric 2 : 5-Dichloroanilino-, 3-Nitro-4-chloroanilino , 2-Nitro *p*-toluidino- and 4-Nitro-*o* toluidino methylenecamphors

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In continuation of our studies, Part XXIV in this series,[1] we have now investigated the rotatory dispersion of the condensation products of oxymethylenecamphors (*d*, *l*, *dl*) and 2 : 5-dichloroaniline, 3-nitro-4-chloroaniline, 2-nitro-*p*-toluidine and 4-nitro-*o*-toluidine.

Influence of Chemical Constitution on Rotatory Dispersion

Rotatory dispersions may be classified as "Simple" or "Complex" according as they can, or cannot, be expressed by Drude's one-term equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$ The condensation products of oxymethylenecamphors and aromatic amines, described here, were found to obey the simple dispersion formula exactly. On plotting $\frac{1}{[\alpha]}$ against λ^2, exact straight lines were obtained (Fig 1)

Out of 430 observations recorded in this paper (Tables III–VI), in as many as 398 cases the difference (o–c) between the observed (o) and the calculated (c) values of specific rotation corresponds to a difference of 0 02° or less in the corresponding angles of rotation In 22 cases this difference lies between 0·02° and 0 03°, and only in 10 cases, most of which are for Hg_{4358} (Mercury violet)—a difficult line to read—this difference lies between 0·03° and 0·05°. All these differences (o–c), not given here for economy of space, are, however, of the nature of casual experimental errors.

Physical Identity of Enantiomers

Pasteur's Law of Molecular Dissymmetry, according to which the *d*- and *l*-forms of a substance possess identical physical properties as regards their magnitude has been found to hold good: the values of the rotatory power of the *d*- and *l*-forms of the compounds in different solvents (Tables III–VI) are identical within the limits of experimental error.

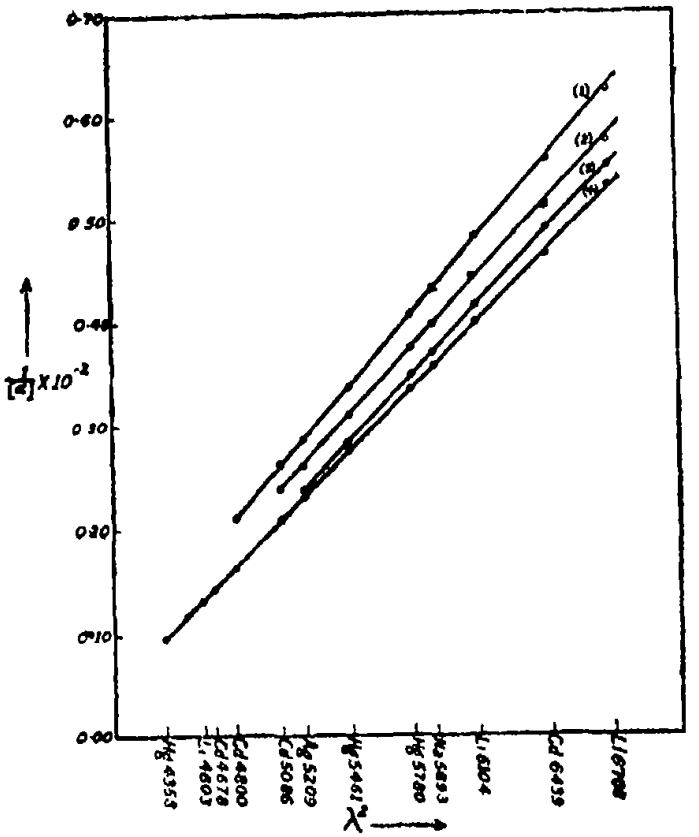


FIG 1

(1) 2-Nitro-*p*-toluidinomethyl ene-*d*-camphor in benzene
(2) 3-Nitro-4-chloroanilinomethyl ene-*d* camphor in chloroform.
(3) 4-Nitro-*o*-toluidinomethyl ene-*d*-camphor in methyl alcohol.
(4) 2 · 5-Dichloroanilinomethyl ene-*d*-camphor in methyl alcohol

EFFECT OF THE NATURE OF THE SUBSTITUENT GROUP ON THE ROTATORY POWER

The polar effect of substituent group is traceable in optical activity.[1,2]

In the present investigation we have studied the effect on rotation of three substituents, Cl, CH_3 and NO_2 groups, which are assigned polarities in accordance with the following polar series[3] deduced from specific inductive capacities: $\bar{O}H$, Cl, Br, I, C_6H_5, $C\bar{H}_3$, $\overset{+}{H}$, CO_2H, CHO, $COCH_3$, CN, $N\overset{+}{O}_2$. From this study it is found that the effect of substituents on the rotatory power can be generally correlated with their polarities as is evident from the account:—

(1) Cl, on account of its negative polarity, lowers the rotatory power of the parent compound as supported by the following observations (Table I):

TABLE I

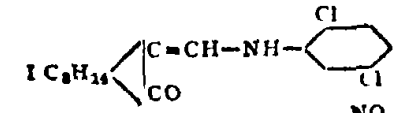
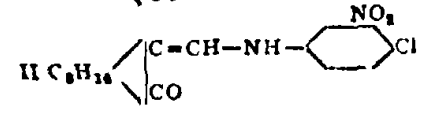
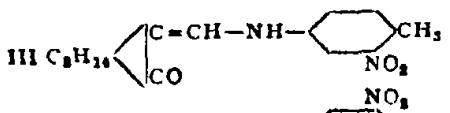
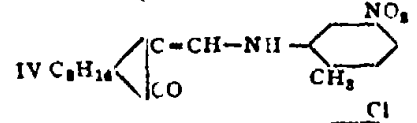
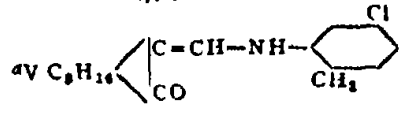
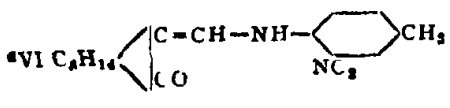
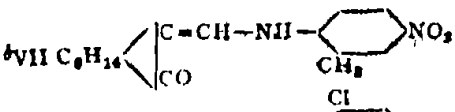
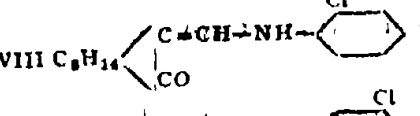
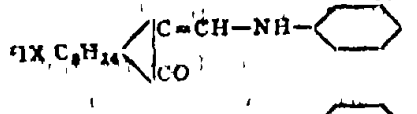
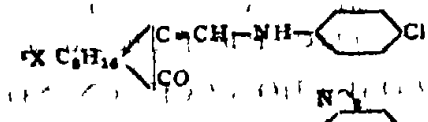
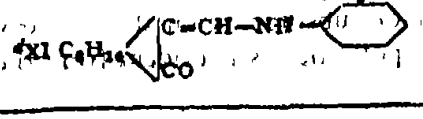
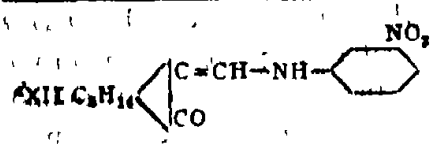
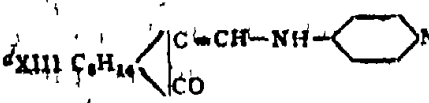
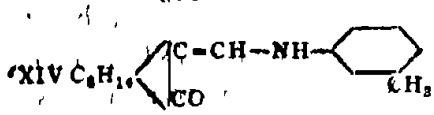
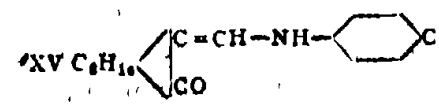
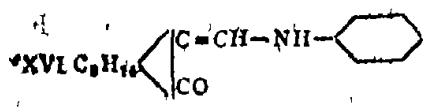
Structural formulæ	$[\alpha]^{35°\,C}_{Hg_{5461}}$					
	MeOH 31 2°	EtOH 25 8°	Acetone 21 5°	Pyridine 12 4°	Chloroform 5 2°	Benzene 2 28°
 I C_8H_{16}	360 0° (60 17)	351·0° (57 76)	352 0° (58 11)	358·0° (59·45)	356 0° (57 76)	344·0° (56·94)
 II C_8H_{16}	390·0 (65·09)	385 0 (66·32)	360·0 (64·45	350 0 (61 69)	327·0 (57·11)	290 0 54·14)
 III C_8H_{16}	388 0 (66 68)	376 0 (66·21)	368 0 (65 54)	362 0 (6 ·2)	330 0 61 26	295 0 (52 39)
 IV C_8H_{16}	350 0 (57 16)	352 0 (57 8)	355 0 (58 58)	370 0 (58·03)	353 0 (56 38	339·0 (55·24)
 V C_8H_{16}	386 0 (62·6)	378 0 (60 7)	380 0 (62 5)	390 0 (63·6)	373 0 (60·4)	351·0 (58 5)
 VI C_8H_{16}	492 9† (65 46)	459 5† (62 44)	464 1† (60·26)	416·4† (57·32)	456 5† (64·18)	390 0 (59 45)
 VII C_8H_{16}	491·6 (70·4)	500·7 (67·43)	522 1 (70·61)	561·5 (70·2)	523·3 (66 63	479 4 (66·71)
 VIII C_8H_{16}	400 2 (64·77)	405·6 (72 23)	380·0 (61 42)	391·2 (63·72)	386 0 (61 79)	364 7 (57 76)
 IX C_8H_{16}	388 5 63·14	384·7 62·47)	388 0 (63·65	374 4 (63 70)	371·4 (61 22)	363 6 60·73)
 X C_8H_{16}	417·7 (75·84)	406 3 (73·2)	401 8 (70 89)	394 4 (68·19)	374·6 (67·66)	369·4 (67·80)
 XI C_8H_{16}	493·1† (57 80)		468·1† (59 07)	424·8† (72·06)	434·7† (45·54	390·2 I (50·36)

TABLE I—*Contd.*)

Structural formula	$[\alpha]^{35°\,C.}_{Hg_{5461}}$					
	MeOH 31·2°	EtOH 25·8°	Acetone 21·5°	Pyridine 12·4°	Chloroform 5·2°	Benzene 2·28°
[XII] 	393·9° (79 36)	..	389·2° (69·47)	367·1° (69·80	350·0° (68·63)	315·6° (57·73)
[XIII] 	510 7 (77·47)	..	519·4 (74 11)	545·0 (79 58)	493·5 (74·49)	437·0 (68·05)
[XIV] 	454·4 (85·21)	439 9° (81 02)	442·3 (82 31)	405 8 (80·48)	384·8 (66·55)	352·6 (71 37)
[XV] 	465 0 (79 56)	440 8 (80·13)	425 8 (78·77)	401·6 (74·13)	401 6 (74·13)	355·4 (66 65)
[XVI] 	480 0 (86·78)	461 3 (81·83)	448·9 (83·06)	433·2 (81 21)	424 6 (78·57)	367·1 (70·71)

* Dielectric constant of the solvent

† Calculated value from the dispersion formula

a B. K. Singh and R. K. Tewari, *Proc Indian Acad. Sci*, 1945, 22 A. 20

b B K Singh and A B Lal, *Ibid*, 1941 12A, 157

c B. K Singh and B Bhaduri, *Ibid.*, 1937, 6A, 340.

d B. K. Singh and T P Barat, *J. Indian Chem Soc*, 1940, 17, 1

e B K Singh, B Bhaduri and T Barat, *Ibid*, 1931, 8, 345

the rotatory power of 2·5-dichloroanilinomethylenecamphor (I) is lower than that of *o*- and *m*-chloroanilinomethylenecamphors (VIII, IX); the rotatory power of 3-nitro-4-chloroanilinomethylenecamphor (II) is lower than that of *m*-nitroanilinomethylenecamphor (XII); and the rotatory power of *o*-, *m*-, and *p*-chloroanilinomethylenecamphors (VIII, IX, X) is lower than that of anilinomethylenecamphor (XVI) in all the solvents. (2) CH_3 group also, on account of its negative polarity, has a lowering effect on the rotatory of the parent compound as is evident from the following observations

p-toluidinomethylenecamphors (XIV, XV) is lower than that of anilinomethylenecamphor (XVI) in all the solvents; the rotatory power of 4-chloro-*o*-toluidinomethylenecamphor (V) is lower than that of *m*-chloroanilinomethylenecamphor (IX) in five solvents but *higher* in pyridine. There are, however, some deviations from the abovementioned generalization: the rotatory power of 4-nitro-*o*-toluidinomethylenecamphor (IV) is lower than that of *m*-nitroanilinomethylenecamphor (XII) in three solvents but *higher* in pyridine, chloroform and benzene; the rotatory power of 5-nitro-*o*-toluidinomethylenecamphor (VII) is lower than that of *p*-nitroanilinomethylenecamphor (XIII) in methyl alcohol but *higher* in acetone, pyridine, chloroform and benzene. (3) On the other hand, the positive-polarity of NO_2 group should raise the rotatory power of the parent compound. This is supported by the following observations (Table I): the rotatory power of 3-nitro-*p*-toluidinomethylenecamphor (VI) is higher than that of *p*-toluidinomethylenecamphor (XV), and the rotatory power of *p*-nitroanilinomethylenecamphor (XIII) is higher than that of anilinomethylenecamphor (XVI) in all the solvents; the rotatory power of *o*-nitroanilinomethylenecamphor (XI) is higher than that of anilinomethylenecamphor (XVI) in all the solvents except pyridine in which it is lower. But in the following three cases the NO_2 group is found to have a lowering effect on the rotatory power: the rotatory power of 3-nitro-4-chloroanilinomethylenecamphor (II) is lower than that of *p*-chloroanilinomethylenecamphor (X); the rotatory power of 2-nitro-*p*-toluidinomethylenecamphor (III) is lower than that of *p*-toluidinomethylenecamphor (XV); and the rotatory power of *m*-nitroanilinomethylenecamphor (XII) is lower than that of anilinomethylenecamphor (XVI) in all the solvents

The effect of polarity of the substituent group is, with minor deviations, thus traceable in optical activity.

The position of the substituent group has also an effect on the rotatory power and is brought out in the following cases: 3-nitro-*p*-toluidinomethylenecamphor (VI), in which the NO_2 group is in the *o*-position to the substituted amino-group, has a higher rotatory power, whereas 2-nitro-*p*-toluidinomethylenecamphor (III) in which it is in the *m*-position to the substituted amino-group, has a lower rotatory power than that of *p*-toluidinomethylenecamphor (XV). Similarly, the rotatory power of *o*-nitroanilinomethylenecamphor (XI) and *p*-nitroanilinomethylenecamphor (XIII) is higher (except in pyridine in the former case), whereas the rotatory power of *m*-nitroanilinomethylenecamphor (XII) is lower than that of anilinomethylenecamphor (XVI) The NO_2 group raises the rotatory power when it is in

the *o*- or *p*-position to the substituted amino-group, whereas it lowers it when it is in the *m*-position.

EFFECT OF THE NATURE OF THE SOLVENT ON THE ROTATORY POWER

The specific rotatory power of these compounds for Hg_{5461} in six solvents is given in Table I. The sequences of decreasing rotatory power are as follows:—2:5-dichloroanilinomethylenecamphor (I): methyl alcohol > pyridine > chloroform > acetone > ethyl alcohol > benzene; 3-nitro-4-chloroanilinomethylenecamphor (II): methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene; 2-nitro-*p*-toluidinomethylenecamphor (III): methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene; 4-nitro-*o*-toluidinomethylenecamphor (IV): pyridine > acetone > chloroform > ethyl alcohol > methyl alcohol > benzene. The sequence of decreasing (or increasing) rotatory power runs in the cases of 3-nitro-4-chloroanilinomethylenecamphor (II) and 2-nitro-*p*-toluidinomethylenecamphor (III) strictly parallel with that of the dielectric constants of the solvents, namely, methyl alcohol (31·2) > ethyl alcohol (25·8) > acetone (21·5) > pyridine (12·4) > chloroform (5·2) > benzene (2·28). A similar but less marked parallelism can be traced in the case of the other two compounds also, namely, the rotatory power of 2:5-dichloroanilinomethylenecamphor (I) is highest in methyl alcohol, which has the highest dielectric constant, and lowest in benzene, which has the lowest dielectric constant, and the rotatory power of 4-nitro-*o*-toluidinomethylenecamphor (IV) is lowest in benzene.

It would, however, seem more rational to compare the rotatory power of a substance with the dielectric constant of its solution, and not of the solvent in which its rotatory power is determined. We have used the values of the dielectric constants of the solvents as we have not at our disposal the values of the dielectric constants of the solutions.

The abovementioned sequences of rotatory power in the different solvents are derived from the rotatory power measurements for Hg_{5461} (Table I). The choice of this wave-length is purely arbitrary as different sequences are obtained for other wave-lengths. For example, in the case of 4-nitro-*o*-toluidinomethylenecamphor (IV) the sequence for Hg_{5461} is pyridine > acetone > chloroform > ethyl alcohol > methyl alcohol > benzene, whereas that for Na_{5896} is pyridine > ethyl alcohol > acetone > methyl alcohol > chloroform > benzene. These effects of dispersion can, however, be eliminated when compounds are found to obey the simple dispersion equation of Drude, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$. The rotation-constant (K) of this one-term equation can

be used as a measure of the absolute rotatory power of the substance. It refers to a wave-length λ, where $\lambda^2 - \lambda_0^2 = 1$ square micron, and it is not very much greater than 10,000 Å U. The longest observed wave-length in our measurements is L'_{5791} and an extrapolation from it to about 10,000 Å U. is easily permissible in view of the linear nature of the dispersion equations obtained from our measurements. We have, therefore, also given in brackets (Table I) the values of K, the rotation-constant, as a measure of the absolute rotatory power of the compounds

It will be seen that the value of K (Table I) in the different runs parallel with that of the dielectric constant of the solvent, in the of 3-nitro-4-chloroanilinomethylenecamphor (II) and 2-nitro-*p* methylenecamphor (III) In the case of the other two compounds (I, IV), there is less strict parallelism. the value of K for 2:5-dichloroanilinomethylenecamphor (I) is lower in ethyl alcohol and higher in pyridine, and for 4-nitro-*o*-toluidinomethylenecamphor (IV) it is lower in methyl and ethyl alcohols than the sequence of the dielectric constants of the solvents warrants it. This further emphasizes that the value of the dielectric constant of the solution rather than that of the solvent should be compared with the absolute rotatory power of the solution.

The compounds listed above in Table II are optically active nitro-dyes. They vary in colour from yellow to orange in the solid state or in alcoholic solution When their alcoholic solution is made alkaline, the colour deepens in the case of the *ortho*- and *para*-nitro compounds (VI and VII,

OF THE POSITION OF THE NITRO-GROUP ON THE COLOUR OF THE DYES

TABLE II

Substances	Colour in the solid state	Colour in ethyl alcohol	Colour in ethyl alcohol in presence of KOH
3-Nitro-*p*-toluidinomethylenecamphor (VI, Table I)	Orange-red	Yellow orange	Port wine red
5-Nitro-*o*-toluidinomethylenecamphor (VII, Table I)	Bright yellow	Yellow	Deep violet
3-Nitro-4-chloroanilinomethylenecamphor (II, Table I)	Bright yellow	Lemon-yellow	Port wine-red
3-Nitro-*p*-toluidinomethylenecamphor (III, Table I)	Lemon-yellow	Lemon-yellow	Yellow-orange
4-Nitro-*o*-toluidinomethylenecamphor (IV, Table I)	Lemon-yellow	Lemon-yellow	Yellowish-light-brown

TABLE III. 2. *5-Dichloroanilinomethylenecamphors*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c.c {*d* / *l*	0·5000 0·5000		0·5000 0·5000		0·5000 0·5000		0·5000 0·5000		0·5000 0·5000		0·5000 0·5000	
Calculated {[α]	$\pm \frac{60\cdot17}{\lambda^2-0\cdot1319}$		$\pm \frac{57\cdot78}{\lambda^2-0\cdot1342}$		$\pm \frac{58\cdot11}{\lambda^2-0\cdot1338}$		$\pm \frac{59\cdot45}{\lambda^2-0\cdot1327}$		$\pm \frac{57,76}{\lambda^2-0,1355}$		$\pm \frac{56\cdot94}{\lambda^2-0\cdot1326}$	
λ₀	0·3631		0·3664		0·3658		0·3643		0·3681		0·3641	
Line λ	Obs [α]		Obs [α]		Obs [α]		Obs. [α]		Obs [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Hg_{4358} ..	+1038·0°	−1032 0°	+1031·0°	−1030·0°	+1030 0°	−1029 0°	+1033·0°	−1034 0°	+1056·0°	−1055 0°	+993 0°	−990 0°
Li_{4603} .	755 0	753·0	742·0	747 0	746 0	746 0	752 0	750 0	755·0	756 0	717 0	718 0
Cd_{4678} .	694 0	693·0	684·0	683 0	682 0	681 0	692·0	691·0	694 0	693·0	662 0	661 0
Cd_{4800} .	612 0	610 0	603 0	601 0	602 0	600 0	609 0	607 0	610 0	608·0	582 0	584·0
Cd_{5086} ..	473·0	472·0	466·0	464·0	464·0	463·0	472·0	471·0	471·0	470·0	452 0	450·0
Cd_{5086} ..	430·0	431·0	422·0	420 0	423 0	421 0	431·0	430 0	426·0	424·0	412 0	411·0
Ag_{5209} .	360 0	362 0	351 0	352·0	352 0	354 0	358 0	361·0	356 0	354 0	344 0	342 0
Hg_{5461} ..	298 0	297 0	288 0	288 0	289 0	290 0	294 0	296·0	290 0	291 0	281 0	281·0
Hg_{5780} .	278·0	280 0	270·0	272·0	271 0	273 0	276 0	276 0	272 0	274 0	264 0	267 0
Na_{5893} ..	249 0	248 0	241 0	244 0	244 0	245·0	246 0	247 0	245 0	246 0	236 0	237 0
Li_{6104} ..	214 0	215 0	207·0	206 0	208 0	209·0	212·0	213 0	208·0	209·0	202 0	203 0
Cd_{6439} ..	188·0	190·0	181 0	182 0	182 0	184 0	186 0	189 0	183·0	185 0	177 0	178 0
Li_{6708} ..	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE IV. *3-Nitro-4-chloroanilmomethylenecamphors*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c.c.	*d* 0·1000	*l* 0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·0500	0·0500
Calculated [α]	$\pm \frac{65\cdot59}{\lambda^2-0\cdot1208}$		$\pm \frac{66\cdot32}{\lambda^2-0\cdot1202}$		$\pm \frac{64\cdot45}{\lambda^2-0\cdot1200}$		$\pm \frac{61\cdot69}{\lambda^2-0\cdot1222}$		$\pm \frac{57\cdot11}{\lambda^2-0\cdot1201}$		$\pm \frac{54\cdot14}{\lambda^2-0\cdot1169}$	
λ_0	0·3561		0·3468		0·3464		0·3496		0·3495		0·3419	
Line λ	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{4800} ..	..	..	..	..	..	..	..	..	..	..	+480·0°	−470·0°
Cd_{5086} ..	+500·0°	−495·0°	+470·0°	−475·0°	+485·0°	−485·0°	+455·0°	−450·0°	+415·0°	−415·0°	390·0	380·0
Ag_{5208} ..	455·0	455·0	435·0	430·0	425·0	425·0	415·0	410·0	380·0	380·0	350·0	350·0
Hg_{5461} ..	380·0	385·0	365·0	370·0	360·0	365·0	350·0	345·0	320·0	315·0	290·0	290·0
Hg_{5770} ..	315·0	320·0	310·0	305·0	305·0	300·0	290·0	285·0	265·0	270·0	250·0	250·0
Na_{5893} ..	300·0	295·0	290·0	285·0	285·0	280·0	275·0	275·0	250·0	250·0	240·0	230·0
Li_{6104} ..	285·0	285·0	280·0	280·0	265·0	260·0	245·0	250·0	225·0	225·0	210·0	221·0
Cd_{6438} ..	235·0	270·0	230·0	225·0	225·0	220·0	210·0	215·0	195·0	190·0	190·0	190·0
Li_{6708} ..	200·0	210·0	195·0	205·0	190·0	195·0	185·0	185·0	175·0	175·0	160·0	170·0
	No mutarotation		No mutarotation		Shows mutarotation; after 24 hrs. $[\alpha]^{35°\,C.}_{Hg5461}$ for *d* = 295·0° and for *l* = 290·0°		No mutarotation		No mutarotation		No mutarotation	

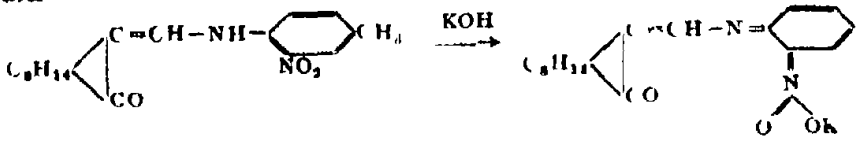
TABLE V. *2-Nitro-p-toluidinomethylenecamphors*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c.c. *d*	0·2500		0·2500		0 2500		0·2500		0·2500		0 1000	
Concentration in gm./100 c.c. *l*	0·2500		0·2500		0·2500		0 2500		0·2500		0·1000	
Calculated [α]	$\pm \frac{66 \cdot 66}{\lambda^2 - 0 \cdot 1271}$		$\pm \frac{66 \cdot 21}{\lambda^2 - 0 \cdot 1215}$		$\pm \frac{65 \cdot 54}{\lambda^2 - 0 \cdot 1206}$		$\pm \frac{65 \cdot 02}{\lambda^2 - 0 \cdot 1190}$		$\pm \frac{61 \cdot 26}{\lambda^2 - 0 \cdot 1127}$		$\pm \frac{52 \cdot 39}{\lambda^2 - 0 \cdot 1201}$	
Calculated λ_0	0·3565		0·3498		0·3472		0·3450		0·3357		0 3465	
Line λ	Obs [α]		Obs [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{6438} ..	..	..	..	..	..	..	..	..	..	..	+475·0°	−470·0°
Cd_{5086} ..	+504·0°	−508·0°	+488·0°	−484·0°	+476 0°	−474 0°	..	..	+422·0°	−418·0°	375·0	375·0
A_{5780} ..	464·0	464·0	440·0	442 0	436·0	436·0	+430 0°	−426 0°	390 0	388·0	345 0	350·0
Hg_{5461} ..	388 0	386·0	376·0	374 0	368 0	368·0	362·0	364·0	330·0	332·0	295·0	290 0
Hg_{5780} .	324 0	322·0	314·0	312 0	308 0	306·0	304 0	302 0	278 0	276·0	245·0	245·0
Na_{5892} ..	302·0	302·0	292·0	290·0	290·0	288 0	288 0	286 0	264·0	264·0	230 0	235·0
Li_{6104} ..	266·0	270·0	266·0	262·0	258·0	260 0	254·0	254 0	2.8·0	238·0	205·0	210 0
Cd_{6439} ..	236·0	234·0	228·0	230·0	226·0	226·0	222 0	224·0	200·0	204·0	180 0	175 0
Li_{6708} ..	210·0	210·0	200·0	202 0	198 0	200·0	196 0	198·0	178 0	180 0	160·0	155·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE VI. *4-Nitro-o-toluidinomethylenecamphors*

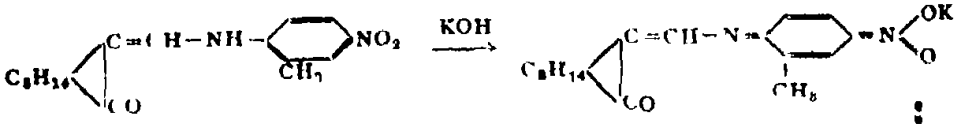
Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c c	*d* 0 5000 *l* 0 5000		0 5000 0·5000		0 5000 0 5000		0 5000 0 5000		0 5000 0 5000		0·5000 0 5000	
Calculated [α]	$\pm \frac{57\ 16}{\lambda^2-0\ 1342}$		$\pm \frac{57\ 8}{\lambda^2-0\ 1339}$		$\pm \frac{58\ 56}{\lambda^2-0\cdot1329}$		$\pm \frac{58\ 03}{\lambda^2-0\ 1420}$		$\pm \frac{56\ 38}{\lambda^2-0\ 1381}$		$\pm \frac{55\cdot24}{\lambda^2-0\cdot1342}$	
λ_0	0·3664		0 3659		0 3645		0 3768		0 3716		0 3664	
Line λ	Obs. [α]		Obs. [α]		Obs. [α]		Obs [α]		Obs [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{5086}	..	..	+461·0°	−464·0°	+461·0°	−464 0°	.	..	+471 0°	−467 0°	+445·0°	−443·0°
Ag_{5461}	+416·0°	−418 0°	420·0	419·0	421 0	423 0	+449 9°	−450·0°	422·0	424 0	404·0	4 2 0
Hg_{5461}	250·0	348 0	352·0	353 0	355 0	354 0	371·0	371·0	353·0	352·0	339·0	336·0
Hg_{4358}	285·0	284 0	289 0	288·0	293·0	292·0	302 0	303 0	287 0	287·0	276·0	276·0
N_{5893}	269 0	270·0	273 0	272·0	272·0	273 0	281·0	284 0	268 0	270 0	260 0	258 0
La_{5184}	240·0	240·0	242 0	243 0	245·0	247 0	253·0	250·0	241·0	239·0	233·0	231·0
Cd_{4416}	203·0	202·0	206 0	205·0	209·0	210·0	215 0	212 0	204·0	201 0	196 0	199·0
La_{4700}	181·0	179·0	183·0	182·0	183 0	186·0	187·0	189·0	179 0	182 0	174·0	176·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

Table II), whereas no such deepening of colour is observed in the case of the *meta*-nitro compounds (III and IV, Table II) This is due to the fact that *ortho*- and *para*-nitro derivatives can change in alkaline solution into the *aci*-form having quinonoid structure as illustrated in the following formulæ



2-Nitro-*p*-toluidinomethylenecamphor (VI, Table II), yellow-orange in alcohol

2 conjugate double bonds (shortest route)
4 conjugate double bonds (longest route)
Port wine red

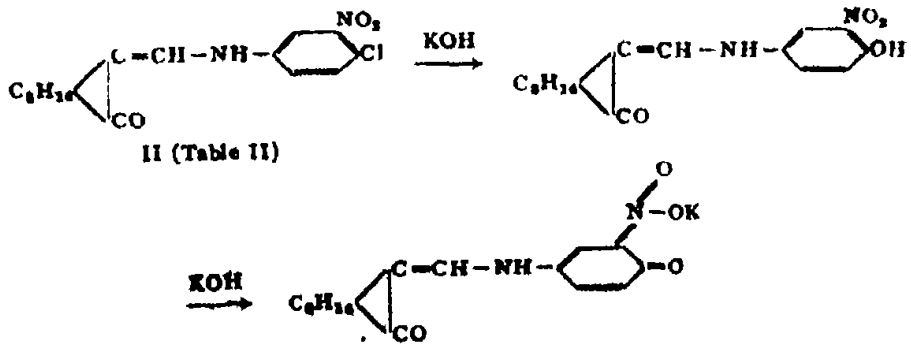


5-Nitro-*o*-toluidinomethylenecamphor (VII, Table II), yellow in alcohol

3 conjugate double bonds (either route)
Deep violet

Further, the chain of conjugate double bonds is longer in the *para*-quinonoid structure than that in the *ortho*-quinonoid structure; this explains the deeper colour of the *para*-nitro compound than that of the *ortho*-nitro compound.

The abovementioned tautomerisation to the *aci*-quinonoid form is not possible in the case of the *meta*-nitro compounds (III and IV, Table II); therefore, there is no change in colour when their alcoholic solution is made alkaline The port-wine red colour of 3-nitro-4-chloroanilinomethylene-camphor (II, Table II), a *meta*-nitro derivative, in alkaline solution can, however, be explained by assuming that the Cl atom, which is rendered labile by the adjacent NO_2 group, is replaced by the hydroxyl group, thus permitting tautomerisation into the *ortho*-quinonoid structure.



II (Table II)

Our results are thus in agreement with the modern views of the influence of chemical constitution on colour [6]

DYEING PROPERTIES OF COMPOUNDS II, III, IV AND VI (TABLE II)

These substances, being acid dyes, have been examined for their dyeing properties on wool from an acid-bath containing 2% sulphuric acid and 10% Glauber's salt. 3-nitro-*p*-toluidinomethylenecamphor (VI) dyes wool a light yellow-orange colour which is fast to washing with soap and to sunlight (30 hours' exposure), 3-nitro-4-chloroanilinomethylenecamphor (II), 2-nitro-*p*-toluidinomethylenecamphor (III) and 4-nitro-*o*-toluidinomethylenecamphor (IV) dye wool light yellow colour which is fast to washing with soap. Sunlight, however, causes fading in these colours to a slight extent after a moderate exposure (12 hours)

EXPERIMENTAL

General Method of Preparation – The *dextro*-forms of the compounds were prepared by adding oxymethylene-*d*-camphor (1 mol proportion), dissolved in ethyl alcohol, to the solution of the free base in acetic acid, when a precipitate was obtained immediately or on keeping. It was then repeatedly recrystallised from ethyl alcohol.

The *lævo*- and *racemic*-isomers were prepared in the same way as the corresponding *dextro*-compounds and had similar crystalline form and solubility.

2:5-*Dichloroanilinomethylene*-d-*camphor*, m.p. 139–140° C., was obtained as crystals with yellow tinge. It is very soluble in acetone, pyridine, chloroform and benzene, less so in methyl and ethyl alcohols, and insoluble in water. (Found: Cl, 21.89; N, 4.05. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87; N, 4.32 per cent.)

2.5-*Dichloroanilinomethylene*-l-*camphor*, m.p. 139–140° C. (Found: Cl, 21·92. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87 per cent.)

2:5-*Dichloroanilinomethylene*-dl-*camphor*, m.p. 136.5–137.5° C. (Found: Cl, 21·87. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-d-*camphor*, m.p. 215–216° C., was obtained as bright yellow rectangular plates. It is soluble in pyridine, less so in acetone, sparingly soluble in chloroform and methyl and ethyl alcohols, very sparingly soluble in benzene, and insoluble in water. (Found: Cl, 10·80; N, 8·19. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10.59; N, 8·37 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-l-*camphor*, m.p. 215–216° C. (Found: Cl, 10·77. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59 per cent.)

3-Nitro-4-chloroanilinomethylene-dl-*camphor*, m p. 204–205° C. (Found Cl, 10·79 $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59 per cent)

2-Nitro-p-*toluidinomethylene*-d-*camphor*, m p. 193–194° C, was obtained as long lemon-yellow rectangular plates It is soluble in pyridine, moderately soluble in acetone, chloroform and methyl and ethyl alcohols, sparingly soluble in benzene, and insoluble in water (Found: N, 8 73 $C_{18}H_{22}O_3N_2$ requires N, 8 92 per cent.)

2-Nitro-p-*toluidinomethylene*-l-*camphor*, m p 193–194° C (Found N, 8·75 $C_{18}H_{22}O_3N_2$ requires N, 8 92 per cent)

2-Nitro-p-*toluidinomethylene*-dl-*camphor*, m p. 181–182° C (Found N, 8 72 $C_{18}H_{22}O_3N_2$ requires N, 8 92 per cent.)

4-Nitro-o-*toluidinomethylene*-d-*camphor*, m p 137 5–138·5° C, was obtained as lemon-yellow needles It is very soluble in pyridine, chloroform, acetone and benzene, less so in methyl and ethyl alcohols, and insoluble in water (Found N, 8 71 $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent)

4-Nitro-o-*toluidinomethylene*-l-*camphor*, m p 137 5–138 5° C (Found N, 8 73 $C_{18}H_{22}O_3N_2$ requires N, 8 92 per cent)

4-Nitro-o-*toluidinomethylene*-dl-*camphor*, m p 139–140° C (Found N, 8 74 $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent)

The rotatory power determinations were carried out in a 2-dcm jacketed tube at 35° C The value of λ_0, calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm

Summary

1 The rotatory dispersion of optically active forms of 2: 5-dichloroanilino-, 3-nitro-4-chloroanilino-, 2-nitro-*p*-toluidino- and 4-nitro-*o*-toluidinomethylenecamphors has been investigated in six solvents for the visible spectrum (λ_{6708} to λ_{4358}), and found to obey the Drude's one-term equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$; it is therefore simple

2. Within the limits of experimental error the *d*- and *l*-forms of these compounds possess identical rotatory power.

3. The effect of the polarities (as deduced from specific inductive capacity) of Cl, CH_3 and NO_2 groups on the rotatory power has been studied With minor deviations, Cl and CH_3 groups, being negative, lower the rotatory power, whereas NO_2 group, being positive, raises the rotatory power. Thus the polar effect of substituent groups is traceable in optical activity

4 Subject to minor deviations, the sequence (decreasing or increasing) of the rotatory power of these compounds runs parallel with that of the dielectric constants of the solvents in which the rotatory power is determined.

We wish to make grateful acknowledgement to the University of Allahabad for the grant of facilities for carrying out this investigation.

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FURTHER STUDIES ON THERMAL REPULSION

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(Communicated by Dr L. A. Ramdas, F.A.Sc.)

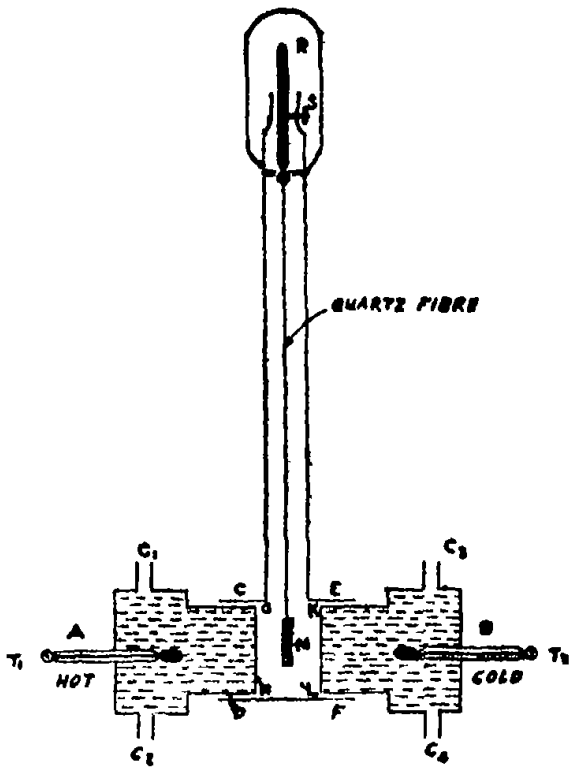
1 Introduction

Ramdas and co-workers pointed out early in 1931 that both above and below a heated plate there is a dust-free layer of very hot air. Above the plate this layer shoots up through the colder air above in a regular pattern forming what is known as the "shimmering layer" This aspect of the subject has been further developed and discussed in a series of papers [1,2,3]

Below the heated plate, owing to the stable arrangement of the air layers, the convective phenomena are not violent as in the previous case but very much simpler In fact, when matters are so arranged that an air cell (filled with smoke and illuminated suitably) is formed with a hot surface above and a cold surface below and the sides are suitably enclosed, the dark layer is found to be restricted in its scope by a pair of vortices. As the cold lower surface is brought nearer and nearer to the hot surface it is found that the vortices separate towards the two sides leaving a calm layer at the centre where the dark layer attains a maximum thickness, ultimately, when the cold surface approaches the hot one within 2 mm or less the vortices die away completely, all convective phenomena cease, and thermal repulsion has full play. When this "convection-free" state is reached, dust particles are repelled with a uniform velocity as defined by Stokes' Law and are deposited on the cold plate The velocity is found to be proportional to the thermal gradient. These results have been discussed fully in a paper[4] by the present writer. Later, Ramdas and Joglekar[5] studied the movements of oil droplets in a vertical convection-free air cell (between a vertical hot surface and a vertical cold surface) and found that the falling particles being acted upon by gravity vertically and by the thermal repulsive force horizontally, move in straight lines inclined to the vertical from the hot to the cold surface.

In the same paper they have described experiments on the steady deflection of a mica vane suspended parallel to the two surfaces by means of quartz fibre. The mica vane is repelled from the hot towards the cold

surface, the deflections being proportional to the temperature gradient. The apparatus used in the above experiment is shown in Fig. 1.



THERMAL REPULSION APPARATUS

FIG 1

A temperature gradient is maintained between the faces GH and KL of the vessels A and B which are kept at the desired temperatures by circulating hot and cold water respectively through the pipes C_1, C_2, C_3 and C_4; T_1 and T_2 are thermometers. The vessels A and B slide in the outer piece CEFD so that the distance between GH and KL may be adjusted as desired. The joints at C, D, E and F are made air-tight by means of a mixture of bees-wax and rosin. The mica piece M is suspended by means of a fine quartz fibre as shown in the figure. As soon as the face GH becomes warmer than KL, M is deflected to the right, the deflection being proportional to the temperature difference when the air cell is thin enough to be convection-free, as it is always arranged to be in all the experiments to be described hereafter. The deflections are measured by means of a microscope focussed on the lower end of the quartz fibre and having a suitable scale in the eye-piece.

The experiments of Ramdas and Joglekar were made at atmospheric pressure At the suggestion of Dr Ramdas the present writer undertook the detailed investigation of thermal repulsion at different pressures ranging from atmospheric pressure to 10^{-4} cm of Hg. The influence of the size of the gap between the hot and cold surfaces, effect of different gases, etc , have also been investigated over the entire range of pressure referred to above The results so far obtained are discussed in the present paper

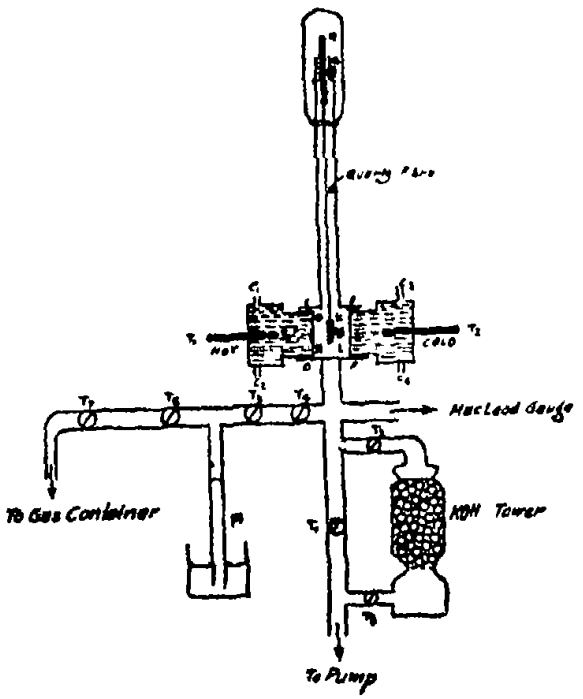
2 Experimental Arrangements

The apparatus shown in Fig. 1 was found to be very convenient for the present work The inter-space GH KL was provided with two diametrically opposite glass windows through which a beam of light coming nearly perpendicular to the plane of the diagram from below illuminated the junction of the quartz fibre and the mica piece. The gap was also provided at the top with an inlet tube for evacuation and introducing other gases For reducing gas pressure a Gaede High-Vacuum Pump was used A specially constructed MacLeod gauge designed to measure pressures in the range 8×10^{-3} cm of Hg to 10^{-4} cm of Hg was used. Pressures higher than 8×10^{-3} cm. were measured directly with a vertically travelling microscope focussed on the top of the mercury column in the MacLeod gauge when its Hg reservoir is kept in the lower position Gas pressures were controlled during experiments by running the pump until the desired pressure was reached and by closing the stopcock between the apparatus and the pump Gases were dried by allowing them to stand in tubes containing phosphorous pentoxide before being drawn into the experimental chamber The temperatures of the hot and cold surfaces could be maintained constant to within $0{\cdot}1^{\circ}$ C , but actual temperature readings were always taken

The general experimental arrangement is shown in Fig 2.

The procedure followed in introducing a given non-corrosive gas was as follows :—T_2 and T_3 were kept closed T_1, T_4, T_5, T_6 were opened and the air was pumped out until the pressure fell to about 10^{-4} cm as indicated by the gauge. Then T_1, T_4, T_5 and T_6 were closed T_7 was opened and gas was admitted into the P_2O_5 tube between T_6 and T_7. T_7 was closed and the gas allowed to stand in the tube for 15 minutes. Then T_6 was slightly opened and a small quantity (as indicated roughly by the fall of Hg in the manometer M) of gas let into the space between T_6 and T_3 Then T_6 was closed and T_5 opened so that gas filled the space between T_5 and T_4. Then T_5 was closed and T_4 opened so as to admit the gas into the experimental chamber. This precaution in introducing the gas was necessary in order to avoid the

mica vane being thrown into violent oscillations. After introducing the gas, it was pumped out. In this way, the apparatus was washed with the gas under experiment several times before the final filling was done. The thermal repulsion at different pressures was then observed. In the case of



EXPERIMENTAL ARRANGEMENT.

FIG. 2

corrosive gases the KOH tower was used for protecting the pump To pump out the gases, T_1 was closed and T_2 and T_3 were opened. This was continued till the pressure fell to about 1 mm of Hg The tower packed as it was with small KOH tablets offered a large resistance to pumping So to obtain lower pressures T_2 T_3 were closed and T_1 opened, the small residual gas not being expected to cause appreciable damage to the pump

To enable sufficiently low pressures to be attained wide-bored glass-tubing was used for connecting the different parts of the apparatus and rubber-tubing avoided as far as possible

3 VARIATION OF THERMAL REPULSION WITH PRESSURE IN AIR

Fig 3 represents a typical curve showing the dependence of thermal pressure on the gas pressure. The distance between the hot and cold surface was 5 mm. The mica vane was in the middle of the gap. δ is the deflection

in divisions of the microscope eye-piece scale. ΔT is the difference of temperature between the surfaces The length of the quartz fibre was 20 65 cm and the mass of mica 5·8 mgm. The dimensions of the vane were 0·742 cm.

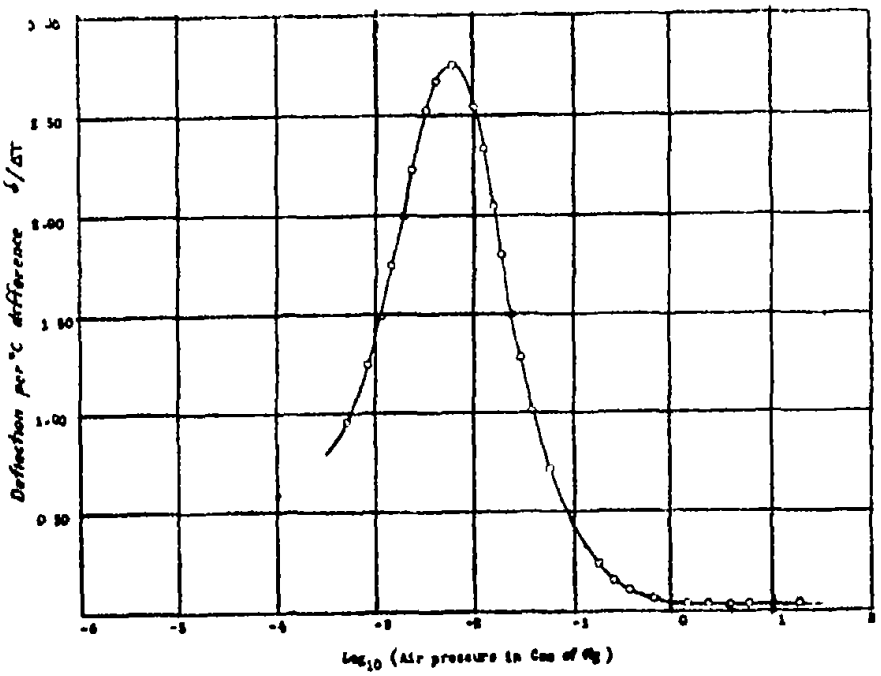


FIG. 3

(length) and 0 328 cm. (breadth) One division in the microscope scale equals 1/20 mm. Unit value of $\delta/\Delta T$ therefore corresponds to a thermal pressure of $5{\cdot}659 \times 10^{-8}$ dynes per cm.[2]

It will be seen that the deflection is very small at high pressures, but increases to a maximum as the air pressure is reduced to $6{\cdot}3 \times 10^{-3}$ cm of Hg The deflection decreases thereafter with further decrease of air pressure

4 Variation of Thermal Repulsion with Temperature Difference

To study the dependence of thermal repulsion on ΔT a gap of 2·5 mm. was used The mica vane was placed in the middle of the gap The dimensions and mass of the mica vane as also the length of the suspension were the same as before. The air pressure was maintained at $6\ 5 \times 10^{-3}$ cm. of Hg. The results are given in Table I δ is the deflection of the vane, δ when plotted against ΔT will be seen to be proportional to the temperature difference. This proportionality is used in the succeeding sections to reduce the deflections for $\Delta T = 1°$ C.

TABLE I

ΔT in °C .	0·0	3 3	3·5	4 2	5·3	7·65
Deflection δ ..	0 0	9·0	7·8	10·5	11·6	18·5

5 VARIATION OF THERMAL REPULSION WITH THE POSITION OF THE MICA VANE IN THE GAP

The mica vane and the suspension used for this experiment were the same as before The gap between the hot and the cold surfaces was 7·5 mm. The vane was initially placed at different positions along the axis of the gap and corresponding values of $\frac{\delta}{\Delta T}$ and p were obtained for each of these positions

The results are given in Table II $\left(\frac{\delta_m}{\Delta T}\right)$ is the maximum value of $\frac{\delta}{\Delta T}$ and the distance referred to is that of the vane from the hot surface The third row of the table gives the air pressure corresponding to the maximum deflection or what may be called the optimum air pressure. It will be seen that both $\frac{\delta_m}{\Delta T}$ and the optimum air pressure increase in value as either the hot or the cold surface is approached

TABLE II

Distance from hot surface in mm	1·30	2 5	4 25	5 5	6 9
$\delta_m/\Delta T$.	2 25	2 15	2·10	2 23	2 65
$p \times 10^3$ cm of Hg .	5 62	4 17	4 27	4 79	7 59

6 EFFECTS OF VARYING THE WIDTH OF THE GAP

The experiment described in Section 5 was repeated with a number of gaps using the same vane and suspension as before The whole of the data cannot be given here for considerations of space. It was however observed that if we restrict our attention to the same value of $\frac{Z}{g}$ (where Z is the distance of the vane from the hot surface and g the width of the gap) then the maximum deflections and the corresponding optimum pressures showed some interesting features. These are given in Table III for the case $\frac{Z}{g}$ nearly equal to 0·5. g is the gap in mm It will be seen that $g \times \frac{\delta_m}{\Delta T}$ (where δ_m is the maximum deflection) has a mean value of 15·53. It increases from 12·9

for a small gap of 1·25 mm. to 17 0 for a gap of 10 mm but remains constant for bigger gaps.

Again one notices a gradual but slight increase in the value of $g \times \rho_m$.

TABLE III

Gap in mm. ..	1·25	2 5	5	7 5	10 0	11 25	15 0	20·0
Gap × ρ_m × 10^2 ..	3 13	3·46	3·15	3·20	3·54	3·58	3 77	3·55
Gap × $\delta_m/\Delta T$ ..	12·9	13·1	14·5	15 8	17 0	17 5	18 5	17 0

7 VARIATION WITH THE AREA AND PERIMETER OF THE VANE

TABLE IV

$-\text{Log}_{10} p$ ..	1	1 4	1 6	1 8	2 0	2 2	2 4	2 6	2·8	3·0	3·2	3·4
$(\delta/\Delta T)_1$ / $(\delta/\Delta T)_2$	1·32	1 18	1·18	1 20	1·24	1 24	1·23	1·23	1·4	1·37	1 4	1·56

Rectangular mica vanes were used for this purpose. Table IV refers to a comparison of results with two mica vanes over a wide range of air pressures. The first had an area of 100 mm^2 Its dimensions were 1 cm × 1 cm. and mass 18 4 mgm The length of the suspension was 25 2 cm The other vane had an area of 45 mm.^{2} Its dimensions were 1 5 cm × ·3 cm. and mass 9 9 mgm The length of the suspension was 25 5 cm The first row in Table IV gives the air pressure and the second row gives the ratio of the deflections in the two cases This ratio is seen to be fairly constant over the wide range of pressures experimented with This indicates that thermal forces bear a sensibly constant ratio at all pressures.

Table V gives the values of $\frac{m}{l} \times \frac{\delta_m}{\Delta T}$ for a number of mica vanes, m, l being respectively the mass and the length of the suspension $\frac{m}{l} \times$

TABLE V

Perimeter mm. .	14·0	21 2	33 4	36·0	40·0
Area in mm^2 ..	12 0	23 7	27·0	45 0	100 0
$\frac{m}{l} \times \frac{\delta_m}{\Delta T}$ ..	0·45	0·79	0 91	1 34	2 86

is proportional to the maximum thermal force. The table also gives the perimeter and the area of the vanes. The thermal force seems to be proportional to the area. There is no simple relation between the thermal force and the perimeter. Thermal force does not, therefore, appear to be an edge effect. It is area effect, under the "convection-free" conditions of our experiments.

8 Experiments with Mica and Aluminium Vanes

To study the effect of the conductivity of the material of the vane, the experiment was done with a mica vane and later with an aluminium vane Both had nearly the same area The dimensions of the Al vane were 1 05 × 0 95 cm. Its mass was 48 mgm and suspension length 22·0 cm. The mica vane had dimensions 1 cm. × 1 cm. Its mass was 18 4 mgm, and the suspension length 25·2 cm. Fig. 4 represents the results obtained.

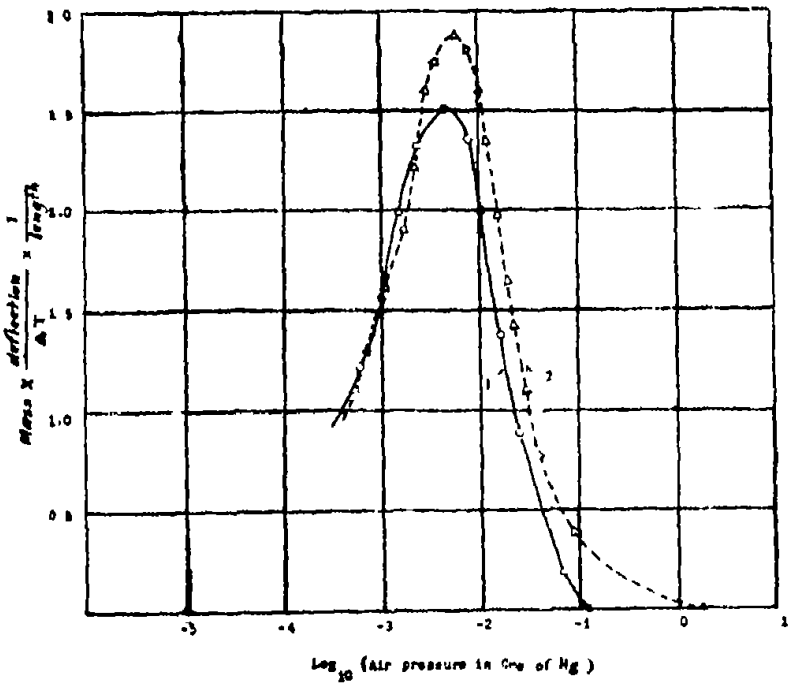


Fig 4

Curve 1 refers to aluminium and curve 2 refers to mica. The force on aluminium is slightly less than on mica. In comparison with the ratio of thermal conductivities of the two materials $\left(\frac{\text{conductivity of aluminium}}{\text{conductivity of mica}}\right.$ $= \frac{514}{0018} = 285{\cdot}6\Big)$, the change in thermal repulsion seems to be slight.

9 Variation with Different Positions of the Vane along a Diameter of the Cylindrical Chamber

A series of measurements were made with the mica vane at different positions along a vertical diameter of the chamber, but equidistant from the two surfaces The results obtained showed that there is no appreciable variation with the position of the vane along this direction.

10. Vane Placed with its Plane Perpendicular to the Plane of the Hot or Cold Surface

In Fig. 5, Curve 1 shows the results when the vane is parallel to the hot surface and Curve 2 shows the results when the vane is perpendicular to the

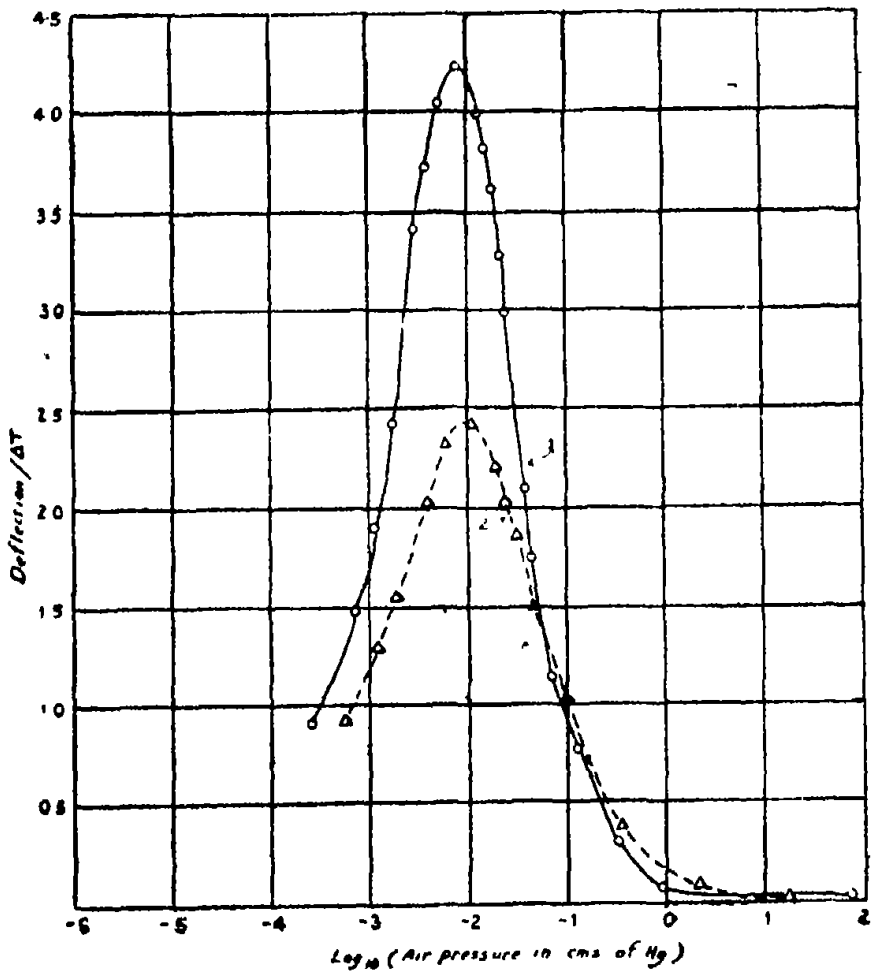


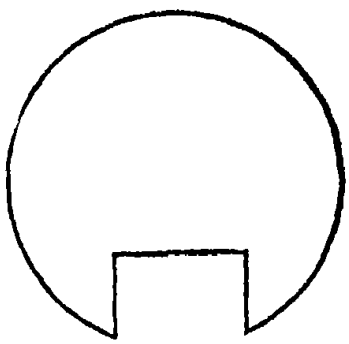
Fig 5.

hot surface. The maximum thermal repulsion in the latter case is roughly half of that when the vane is parallel to the surface

11. Large Aluminium Vane

The diameter of the circular chamber is 7·25 cm In all the previous experiments the area of the vane was very small as compared to the area of the hot or cold surface. To study what happens when the area of the vane

approaches that of the hot surface, an aluminium blade of the shape given in Fig. 6 was used. It is a thin circular disc of radius 3·25 cm. with a rectangular cut 2·5 cm. × 1·5 cm. to allow free space for the glass separating



SHAPE OF THE LARGEST ALUMINIUM VANE USED

FIG 6

pieces placed between the hot and the cold surfaces The area of the vane was 29·44 cm ^{2} The maximum value of $\frac{m}{l}\frac{\delta}{\Delta T} \times \frac{1}{A}$ (which is proportional to the ratio of thermal force to area A of the vane) was found to be 0·024 This compares favourably with the value 0·025 found for an aluminium blade 1 cm. × 1 cm. Thus the proportionality of thermal force to area holds over a very wide range of areas.

12. DIFFERENT GASES

A gap of 5 mm was used In all cases the vane was kept in the centre of the gap. The vane was of mica and had dimensions 742 × ·32 × ·016 cm Its mass was 5 8 mgm and the suspension length = 20·65 cm The results obtained are shown in Fig. 7. It will be seen that as the molecular size increases, the peak becomes lower and at the same time shifts to the low pressure side. In Fig. 8, the values of $\delta_m/\Delta T$ (maximum deflection per degree difference of temperature) are plotted against the mean free path at N T.P. which is inversely proportional to the area of molecular cross-section. The values are the means of two sets of observations The curve is a straight line passing close to the origin In Fig 9, the abscissæ are $\log_{10}$ of the optimum gas pressures. From the graph it can be deduced that

$$56{\cdot}23 \times p_m^{0.10} = 56\ 23 \times p_m^{0.0} \text{ nearly.}$$

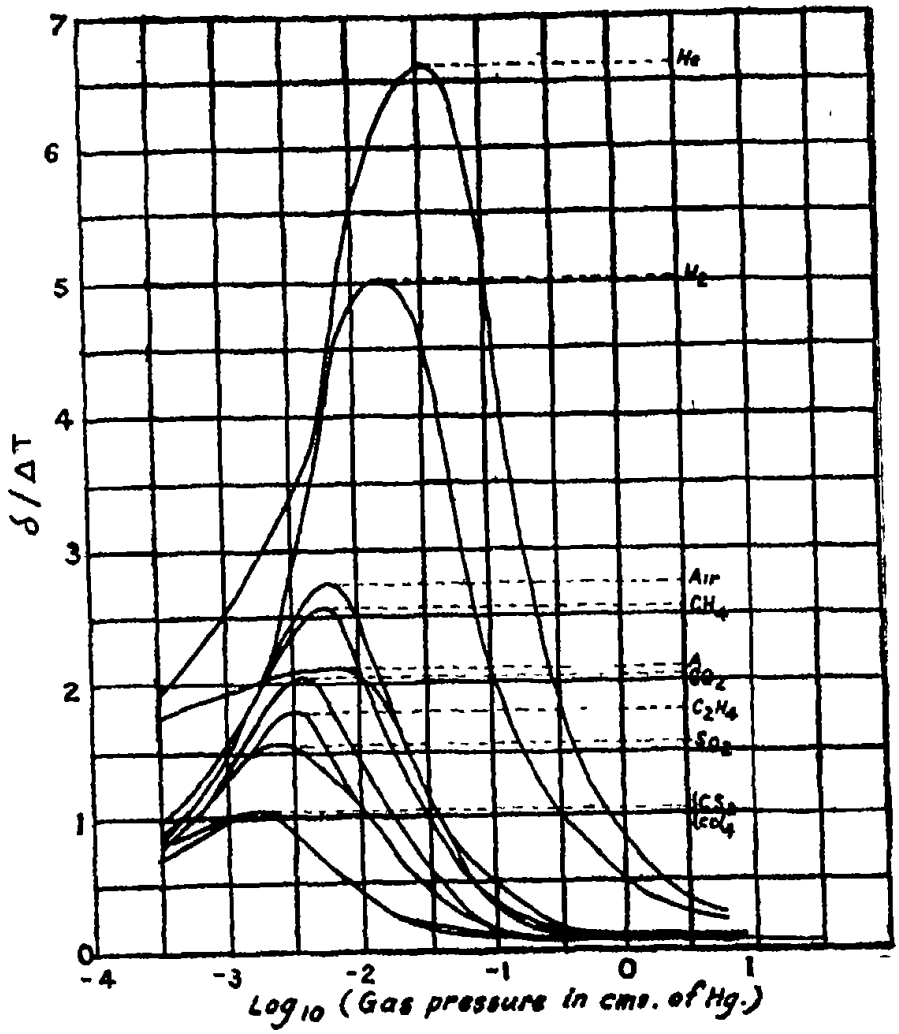


FIG. 7

13. GENERAL DISCUSSION OF RESULTS

(*a*) In the experiments described above, a vertical gas cell is used. As shown in a previous paper by the present author, a vortex motion is present at atmospheric pressure if the gap is not small enough. If the gas pressure is reduced sufficiently, a stage is reached when the vortex motion will cease whatever be the width of the gap. The wider the gap the lower the pressure will have to be reduced to for attaining the "convection-free" state. For the purpose of the present paper, it is quite safe to assume that at pressures below 1 mm of Hg convectional movements are entirely absent. In an air cell without convective movements the air is stratified into vertical strata

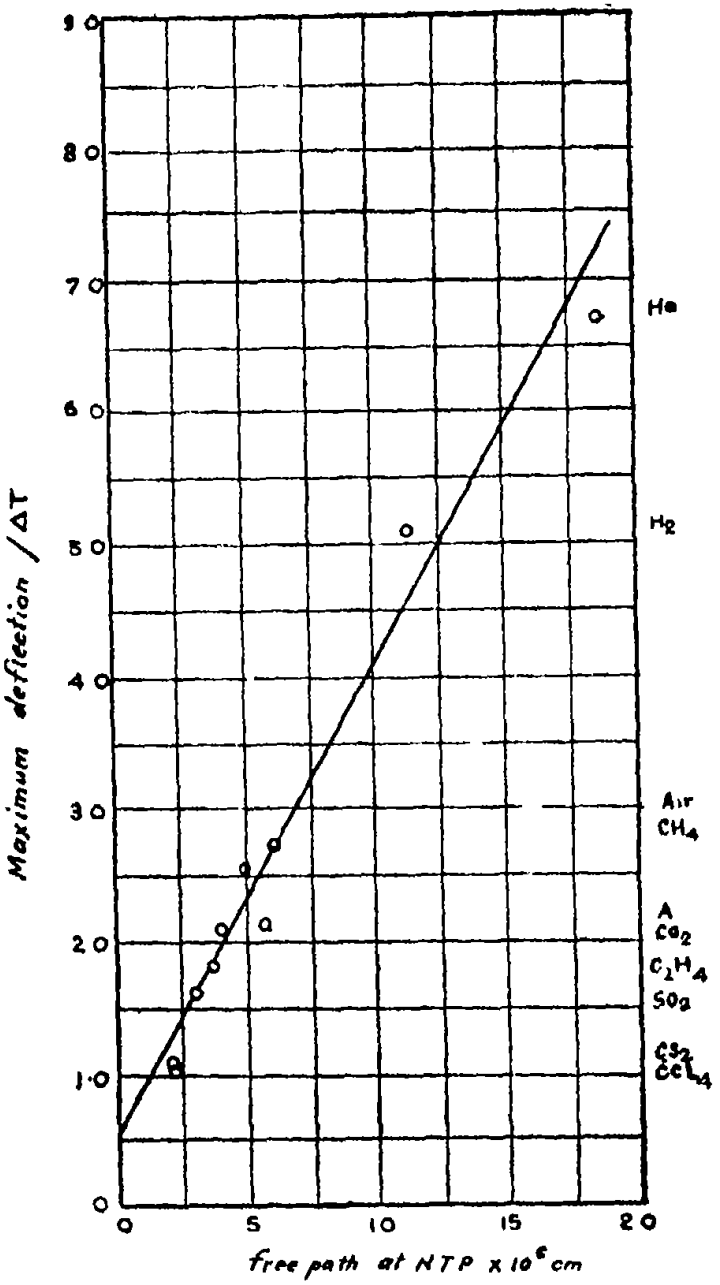


Fig. 8

at different temperatures and the heat conduction proceeds under the ideal conditions imagined in deducing the conductivity formula in the kinetic theory of gases.

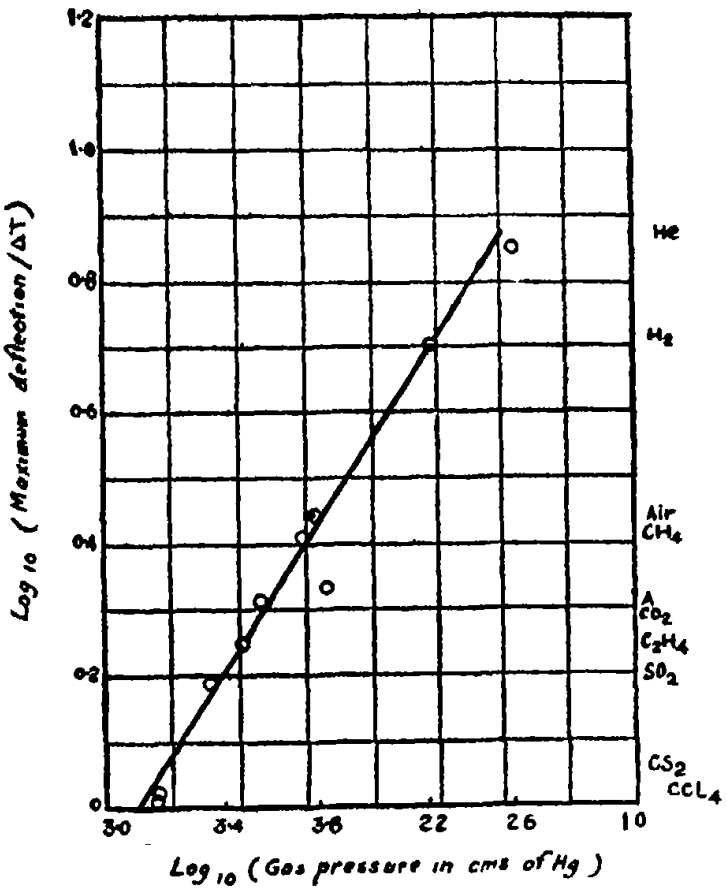


FIG 9

An attempt will now be made to derive an expression for the thermal pressure starting from some elementary considerations and to use it to explain the important features of the phenomenon described in the foregoing sections

In Fig 10 let HH be the hot surface and CC the cold surface. Imagine unit area AB parallel to HH. This area is crossed by the same number of molecules per second in either direction. Denote this number by 'n'. The molecules crossing AB from left to right are more energetic than those crossing AB from right to left. Naturally there will be a net transfer of momentum from left to right across AB. This momentum will clearly be proportional to 'n'. Again the molecules crossing AB from left to right may be supposed to have, on an average, a temperature t_1 appropriate to some such plane as P_1. Similarly we may suppose P_2 to be the equivalent plane on the right-hand side and let the temperature there be t_2 Then the

momentum 'M' transferred across AB in unit time may further be assumed to be proportional to $t_1 - t_2$ or Δt

$$\therefore \quad M \propto n \, \Delta t$$

Now the number 'n' of molecules crossing unit area is known to be proportional to gas pressure 'p'

$$M \propto p \, \Delta t$$

We now observe three things about Δt.

(i) The molecules crossing AB from left to right are coming from different strata between HH and AB. As the pressure of gas is reduced, the mean free path increases, and the proportion of the molecules coming from larger distances from AB increases, the equivalent plane P_1 moving nearer to HH and thus increasing the value of t_1. A similar argument shows that as pressure decreases, P_2 moves towards CC, decreasing the value of t_2. Thus as gas pressure 'p' decreases, the effective temperature difference increases

(ii) Imagine a molecule to travel from the hot to the cold surface Then it suffers $\pi\sigma^2 g\nu$ collisions, where σ is molecular diameter, 'g' the distance between the hot and cold surfaces, and ν is the number of molecules per c c. The degree of equalisation of kinetic energies clearly increases with the number of these collisions and may therefore be assumed to be proportional to

$$a_1 + b_1(\pi\sigma^2 g\nu) + c_1(\pi\sigma^2 g\nu)^2,$$

where a_1, b_1 and c_1 are constants.

Δt will clearly decrease as the degree of equalisation of kinetic energies increases Let us put therefore

$$\Delta t \propto \frac{1}{\text{degree of equalisation of kinetic energies}}$$

$$\text{or} \quad \Delta t \propto \frac{1}{a_1 + b_1(\pi\sigma^2 g\nu) + c_1(\pi\sigma^2 g\nu)^2}$$

But $\nu \propto p$ and therefore we may write

$$\Delta t \propto \frac{1}{a_1' + b_1'(\pi\sigma^2 gp) + c_1'(\pi\sigma^2 gp)^2},$$

where a_1', b_1' and c_1' are constants

This is obviously consistent with the idea in (i).

(iii) Again Δt may be assumed to be proportional to ΔT, the temperature difference between the hot and the cold surfaces.

$$\therefore \quad \text{We put} \quad \Delta t \propto \frac{\Delta T}{a_1' + b_1'(\pi\sigma^2 gp) + c_1'(\pi\sigma^2 gp)^2}$$

But we have seen that $M \propto p\,\Delta t$.

Therefore $$M \propto \frac{p\Delta T}{a_1' + b_1'(\pi\sigma^2 gp) + c_1'(\pi\sigma^2 gp)^2}$$

If we now suppose that a vane of some material is suspended in the position AB, then this vane will experience a thermal pressure proportional to M. We therefore have thermal pressure

$$P = \frac{ap\,\Delta T}{1 + b(\sigma^2 gp) + c(\sigma^2 gp)^2} \tag{1}$$

a, b and c being constants

We will now examine how far (1) explains "the observed results"

It can be shown by differentiating the above with respect to p, that 'P', regarded as a function of 'p', has a maximum at $p = \frac{1}{\sqrt{c}\,g\sigma^2}$ This explains the hump observed in Section 3 The proportionality of 'P' to ΔT (when 'p' is kept constant) described in Section 4 also follows from (1). The optimum pressure

$$p_m = \frac{1}{\sqrt{c}\,g\sigma^2} \tag{2}$$

so that $p_m \times g$ = a constant for a given σ, *i e*, for a given gas. This was the result found in Section 6 If now we substitute this optimum value of 'p' in (1) then the maximum thermal pressure

$$P_m = \frac{(a\,\Delta T)/(\sqrt{c}g\sigma^2)}{2 + \frac{b}{\sqrt{c}}} \tag{3}$$

If the gap is varied, then $P_m \times g$ is a constant This is another result found in Section 6

In Sections 7 and 11 we have seen that the thermal force is proportional to area. This hardly needs any explanation after reading through our derivation of equation (1)

If the vane is thin enough to enable us to suppose that its two sides do not differ very much in temperature, then it is immaterial as to what the material is. This is roughly what we find in Section 8

From equation (1) it will be seen that as the gas pressure p tends to zero the thermal pressure P tends to be equal to $ap\,\Delta T$. This expression is independent of σ and therefore independent of the gas used. Here reference may be made to the work of Lockenvitz.[8] He shows that the thermal pressure

at very low gas pressure is given by

$$P = \frac{p}{4T} \Delta T$$

This is independent of the particular gas used. We thus see that equation (1) gives as a limit the formula of Lockenvitz

Let us now consider results for different gases described in Section 12 The maximum deflection $\delta_m / \Delta T$ (which is proportional to the maximum thermal pressure) was there seen to be proportional to the mean free path at N T P, *i e*, $\lambda \propto \frac{1}{\sigma^2}$

$$\text{Therefore } \frac{\delta_m}{\Delta T} \propto \frac{1}{\sigma^2} \tag{4}$$

This result follows from (3) above

Thus formula (1) represents most of the experimental results.

Consider now the optimum gas pressure p_m as given by (2).

$$p_m = \frac{1}{\sqrt{c g \sigma^2}}.$$

$$\text{But } P_m \propto \frac{1}{\sigma^2}.$$

Therefore on our theory we expect $P_m \propto p_m$ On reference to Section 12 it will be seen however that the verdict of the experiment is

$$P_m \propto p_m^{0.6} \text{ approximately.}$$

Thus in this respect, although the theory given above does predict correctly that p_m increases with P_m, the fit is not quantitative.

(*b*) We shall now consider the experimental results described in Section 5 Mandell and West[7] have shown that the fall of temperature from the hot to the cold surface is not exactly linear. They have shown that the temperature falls more rapidly near the hot and cold surfaces than in the middle. It is natural to expect that the thermal force on the suspended vane will be varying similarly to the temperature gradient in its neighbourhood This explains the larger deflections obtained when the vane approaches either surface.

(*c*) *Explanation of the results in Section* 10 —We have seen that even when the vane is placed perpendicular to the hot surface, there is quite a large thermal repulsion, the maximum value being about one half of what we get when the vane is parallel to the surface. This result may appear

to be rather puzzling at a first glance. One is apt to think that the thermal force when the vane is perpendicular to the hot surface should be vanishingly small. The following considerations, however, show that the deflection

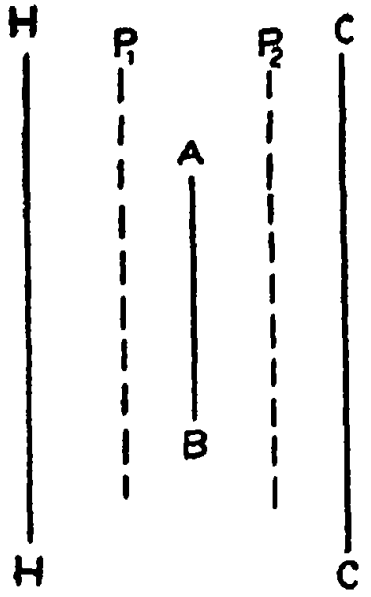


FIG 10

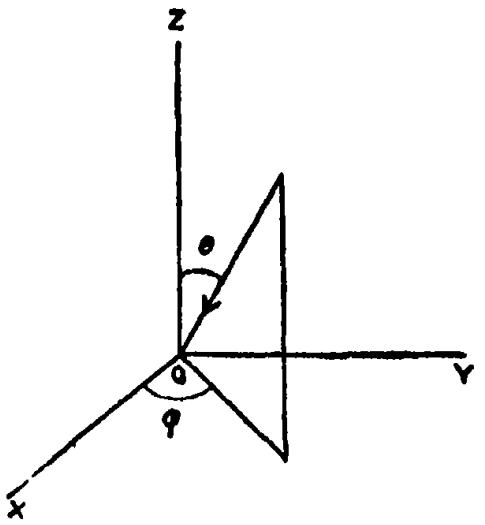


FIG. 11

actually observed in the perpendicular position is to be expected. We make the following assumptions —

(1) Let n be the number of molecules striking or leaving unit area of a solid surface in unit time Then we suppose with Knudsen[8] that the number whose velocity directions lie in a narrow cone of solid angle $d\omega$ whose axis makes an angle ψ with the normal to the surface is given by

$$\frac{n}{\pi} \cos \psi \, d\omega$$

(2) The molecules coming from the hot surface side and the cold surface side have mean velocities C and C_1 respectively, C being $> C_1$, C_0 is the velocity of a molecule corresponding to the temperature T_0 of the vane.

(3) Consider a solid surface at temperature T_0 in contact with a gas. Let the mean temperatures of the incident and reflected molecules be T and T' respectively Then if α is Knudsen's accommodation coefficient,

$$\alpha = \frac{T' - T}{T_0 - T}$$

Let us now suppose that a fraction x of the incident molecules is absorbed and then re-emitted with the temperature T_0 and that the others

are re-emitted without any alteration of temperature. Then the mean temperature of the outgoing molecules $= x T_0 + (1 - x) T$ and this must equal T' Substituting this value of T' in the equation for α we get,

$$\alpha = \frac{x T_0 + (1 - x) T - T}{T_0 - T} = x$$

Let C, C_0 be the molecular velocities appropriate to temperatures T and T_0. We can then sum up this point by saying that *without contradicting Knudsen's* idea of an accommodation coefficient α, we are assuming that of the incident molecules a fraction α is temporarily absorbed and then leaves with velocity C_0, while the remaining molecules go away with unaltered velocity C.

We shall now proceed to calculate P_1 and P_2 which are the thermal repulsion forces per unit area when the vane is parallel and perpendicular respectively to the hot surface.

Choose axes as shown in Fig 11 so that the YZ plane is parallel to the hot surface and the temperature decreases along OX

Calculation of P_1

Suppose that the vane is kept at O with its plane parallel to YZ plane.

The momentum P_1 imparted by the molecules in unit time per unit area of the vane is made up of the following parts on the X side of the YZ plane.

(i) Momentum due to n molecules incident

(ii) Momentum due to $(1 - \alpha) n$ molecules leaving with unaltered velocity.

(iii) Momentum due to αn molecules leaving with velocity C_0. There will be three similar contributions say—(i)', (ii)' and (iii)' due to X' side of the YZ plane. Since (iii) and (iii)' are equal and opposite their joint result $= 0$

Consider (i) and (ii) The result is clearly the same as that of $n + (1 - \alpha) n$ molecules or $n(2 - \alpha)$ molecules being incident. Same is true of (i)' and (ii)'

Thus P_1 = Momentum due to $n(2 - \alpha)$ molecules of velocity C_1 incident on X side of YZ plane and

Momentum due to $n(2 - \alpha)$ molecules of velocity C incident on X' side of YZ.

Write $n' = n(2 - \alpha)$

Now the number of molecules incident along $(\theta, \phi, d\omega)$ in the octant XYZ

$$= \frac{n'}{\pi} \sin\theta \cos\phi \, d\omega$$

$$= \frac{n'}{\pi} \sin^2\theta \cos\phi \, d\theta \, d\phi$$

The momentum due to each molecule of this group parallel to OX

$$= -m c_1 \sin\theta \cos\phi$$

$$P_1 = -4 \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{\pi/2} \left(\frac{n'}{\pi} \sin^2\theta \cos\phi \, d\theta \, d\phi\right) mc_1 \sin\theta \cos\phi \text{ due to}$$

4 octants on the X side of YZ plane

$$+ 4 \int_{\theta=0}^{\pi/2} \int_{\phi=\pi/2}^{\pi/2} \left(-\frac{n'}{\pi} \sin^2\theta \cos\phi \, d\theta \, d\phi\right) (-mc \sin\theta \cos\phi) \text{ due to}$$

the 4 octants on the X′ side of YZ plane

$$= \frac{4n'm}{\pi} \int_0^{\pi/2} \sin^3\theta \, d\theta \left[c \int_{\pi/2}^{\pi} \cos^2\phi \, d\phi - c_1 \int_0^{\pi/2} \cos^2\phi \, d\phi\right]$$

$$= \frac{4n'm}{\pi} \times \frac{2}{3}\left(c\frac{\pi}{4} - c_1\frac{\pi}{4}\right)$$

$$= \tfrac{1}{3} n'm(c - c_1)$$

$$= \tfrac{1}{3} n(2 - \alpha) m(c - c_1) \text{ since } n' = n(2 - \alpha)$$

Calculation of P_2

Suppose the vane to be placed at O with its plane parallel to ZX plane.

P_2 is made up of the following parts:—

(i) Momentum due to n molecules incident on both sides of the vane

(ii) Momentum due to $n(1 - \alpha)$ molecules diffusely leaving the vane without any alteration of the incident velocity on both sides of the vane.

(iii) Momentum due to αn molecules diffusely leaving either side with velocity C_0.

The effect of (iii) is clearly zero Regarding (ii) it can be shown by considering any single group of incident molecules that on leaving diffusely they impart a momentum perpendicular to the vane Further there is symmetry about the ZX plane and therefore the net result is zero.

$\therefore$ P_2 is due to (1) only.

$\therefore$ $P_2 = -4\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{\pi/2}\left(\frac{n}{\pi}\sin^2\theta\sin\phi\,d\theta\,d\phi\right) mc_1 \sin\theta\cos\phi$ due to the 4 octants on the X side of YZ plane

$+4\int_{\theta=0}^{\pi/2}\int_{\phi=\pi/2}^{\pi}\left(\frac{n}{\pi}\sin^2\theta\sin\phi\,d\theta\,d\phi\right)(-mc\sin\theta\cos\phi)$ due to the 4 octants on the X' side of the YZ plane

$$= -\frac{4nm}{\pi}\int_0^{\pi/2}\sin^3\theta\,d\theta\left[c_1\int_0^{\pi/2}\sin\phi\cos\phi d\phi + c\int_{\pi/2}^{\pi}\sin\phi\cos\phi d\phi\right]$$

$$= -\frac{4nm}{\pi}\times\frac{2}{3}\times\left[\frac{c_1}{2}-\frac{c}{2}\right]$$

$$= \frac{1}{3}\frac{nm}{\pi}(c-c_1).$$

$\therefore$ We have $\frac{P_1}{P_2} = (2-\alpha)\frac{\pi}{2}$

If we suppose that $\alpha = 1$, then $\frac{P_1}{P_2} = \frac{\pi}{2}$

If $\alpha = 0$, $\frac{P_1}{P_2} = \pi$

The experimental values obtained so far for α range from 1 to about 2 4

The above results suggest that we have here a new experimental method of investigating the accommodation coefficient

Summary and Conclusion

Using a suspended vane between a hot and a cold surface, a study has been made of thermal repulsion under ideal 'convection-free' conditions. The dependance of the force on area, orientation and material of the vane, size of the gap, the position of the vane relative to the gap as also the nature of the gas has been studied. An explanation of the observed effects has been offered It has also been shown that the variation of thermal repulsion when the vane is parallel and perpendicular respectively offers a new experimental method of investigating the accommodation coefficient.

In conclusion, the author desires to express his indebtedness to Dr. L. A. Ramdas for suggesting the problem and for his interest in the work. The

author also wishes to thank the Director-General of Observatories for permission to work in the Laboratory of the Meteorological Office at Poona. The author also wishes to place on record his thanks to Prof. M G. Mahajan of the Nowroji Wadia College, Poona, for the loan of a megavac pump and to Prof. B V. Bhide of Sir Parashurambhau College, Poona, for facilities given in the preparation of gases

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DETERMINATION OF THE ELASTIC CONSTANTS OF ISOTROPIC MEDIA: A NEW METHOD

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Received March 5, 1946

1 Introduction

The determination of the elastic constants of isotropic substances by dynamical methods has been the subject of investigation by several workers. In most of such methods, the material was used in the form of a rod and ultrasonic waves were transmitted through it by attaching a piezoelectric quartz to one of the ends. Rohrich[1] made a complete determination of the velocity of ultrasonic waves in steel, brass, copper, aluminium and glass. His experiments were continued by Schoeneck[2] who investigated the elastic longitudinal vibrations in single crystals.

More exact determinations of the elastic constants of transparent bodies were carried out by Schæfer and Bergmann.[3] In this method, both longitudinal and shear waves are excited and the corresponding diffraction patterns observed The method has been extended also to opaque substances.

It was recently observed[4] in this laboratory that characteristic thickness shear modes could also be transmitted through the crystal plates and communicated to liquids in the form of consequential longitudinal strains This has suggested the possibility of exciting shear modes in thin plates of isotropic substances as well and detecting them by optical methods if they could similarly be communicated to a liquid

2 Experimental Method and Observations

Using a tourmaline wedge with a frequency range of 3 to 16 megacycles per second, the characteristic transmission frequencies of several plates of glass, steel, brass and platinum have been studied by the method of ultrasonic diffraction, the details of which have been described in earlier papers.[5] Plates of different sizes and of the same thickness have been examined in each case with a view to see if the size has any effect on the intensity of the shear modes In order to avoid errors due to the mounting, the wedge is chosen to be a size smaller than the smallest of the specimens used. Both the longitudinal and shear fundamental frequencies could easily be detected and

measured in transmission if the plates chosen are sufficiently thin and small. The elastic constants C_{11} and C_{44} are then evaluated Using the well-known relations of transformation, the Young's modulus y and the rigidity modulus n may be obtained for each material In the case of glass the values thus obtained are compared with the values obtained by separate static experiments on the same specimen in this laboratory. Comparison for the rest is effected by taking the values from standard tables. It may be noted here that practically all the substances showed an increase in intensity of shear modes with smaller areas of the specimen plates This supports our view that shear modes are communicated as corresponding longitudinal strains to the adjoining liquid due to a coupling effect arising in these cases from the finite size of the plates The shear modes are comparatively weak in soft metals like brass whereas they are very bright in glass and steel, sometimes being equal in intensity to the longitudinal ones. The fundamental frequencies of the longitudinal and shear modes and the calculated values of C_{11} and C_{44} are given in Table I for different materials.

TABLE I

Material	Thickness in mm	Fundamental frequency of longitudinal mode Mega cycles per second	Fundamental frequency of torsion mode Megacycles per second	Density	$C_{11} \times 10^{-10}$ dynes/cm.^{2}	$C_{44} \times 10^{-10}$ dynes/cm.^{2}
Glass ..	0·93	3 22	1 40	26·02	93 2	17·6
Steel .	0 64	4 80	2 60	7 502	287·0	84·0
Brass	0 58	4 20	1·745	8 56	203·0	35·0
Platinum .	0·16	13·30	5 335	20·99	380·2	61·1

The values of y and n deduced from the above data along with the experimental static values of glass and the standard values taken from tables in the other cases are given in Table II

TABLE II

Material	Authors' results		Static values	
	y	n	y	n
Glass .	4 80	1·76	4·60	1 80
Steel ..	21·71	8 40	19 to 21	7·7 to 8·3
Brass	9 77	3 50	9 7 to 10·2	3 5
Platinum .	17·16	6 11	16 80	6·10

The unit is 10^{11} dynes per cm.^{2}

3 Discussion

The smallest size of the plate used in the above investigation is 6 mm. square. The method is simple and sufficiently accurate, being particularly suitable for substances available only as small bits The possibility of investigating the elastic properties of precious metals, alloys and other such materials under varying physical conditions is obvious. The exact mechanism by which the shear mode in the plate is communicated as a longitudinal wave to the liquid medium is of theoretical interest and requires to be further investigated Examination of plates of different sizes has shown that edge coupling of the plates is probably the cause

4. Summary

A new method of determining the Young's modulus and the rigidity modulus of isotropic materials using ultrasonic frequencies has been described. Results obtained with glass, steel, brass and platinum by such a method compare well with the standard values Only a small plate of about 6 mm. square of the material is all that is required and hence the method is capable of being utilized under varying physical conditions in respect of rare and precious specimens

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OPTICAL ACTIVITY IN CRYSTALS: APPLICATION OF GROUP THEORY

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1 Introduction

A phenomenological description of all physical properties of crystals which can be represented by a tensor can be given by simple group theoretical methods. The number of independent constants needed to describe the photo-elastic, elastic and optical properties of each of the 32 crystal classes was thus derived by Bhagavantam (1942) Piezo-electricity was similarly dealt with by Bishambhar Dayal Saksena (1944). The author (1945) has independently extended the method to the cases of piezo-electricity and electro-optical Kerr effect. In this note, the case of optical activity is dealt with

2 Optical Activity

The scalar parameter g which represents the optical activity or rotation per unit thickness of the crystal in the direction l, m, n, is given by

$$g = g_{11} l^2 + g_{22} m^2 + g_{33} n^2 + 2 g_{23} mn + 2 g_{31} nl + 2 g_{12} lm,$$

where g_{ik} $(i, k = 1, 2, 3)$ are the components of the gyration tensor which is known to be symmetric These six components which describe the optical activity in the most general case of a triclinic crystal, reduce to a smaller number as other symmetry elements are introduced. It is an experimental fact that the rotation of plane of polarization is independent of the sense of travel, but the rotation of plane of polarization changes sign by the application of a symmetry operation involving a reflection and remains unchanged by a mere rotation about any axis In order, therefore, to find the number of independent constants required to specify the gyration tensor, we should find the number of independent and orthogonal linear combinations of g_{ik}'s which will transform under each symmetry operation characteristic of the crystal class so as to remain invariant if the symmetry operation is a pure rotation and change sign if the symmetry operation is a rotation-reflection. The character appropriate to the gyration tensor is the same as that used in

earlier references in respect of symmetric tensors of second order and is $4\cos^2\phi \pm 2\cos\phi$. By applying the well-known theorem for finding the number of combinations that will occur under the appropriate irreducible representation, we obtain

$$n_i = \frac{1}{N}\sum_j h_j \chi_j'(R)\,\chi_i(R)$$

where $\chi_j'(R) = 4\cos^2\phi \pm 2\cos\phi$ and $\chi_i(R) = \pm 1$,

according as R is a pure rotation or a rotation-reflection The summation extends over all the symmetry elements characteristic of the crystal class under investigation

3 Results and Discussion

Applying the above formula, it can immediately be seen that the 11 classes with a centre of symmetry (C_i, C_{2h}, D_{2h}, C_{4h}, D_{4h}, S_6, D_{3d}, C_{6h}, D_{6h}, T_h, O_h) exhibit no optical activity Of the remaining 21 classes, six more (C_{4v}, C_{3v}, C_{3h}, D_{3h}, C_{6v}, T_d) do not show optical activity and the others have constants ranging from six to one The actual numbers are given below and in all cases, they agree with the numbers derived directly (Szivessy, 1928, Wooster, 1938)

C_1	6
C_2	4
D_2	3
C_s, C_4, S_4, D_4, C_3, D_3, C_6, D_6	2
C_{2v}, D_{2d}, T, O	1

It is with great pleasure that the author offers his grateful thanks to Prof S. Bhagavantam for his kind encouragement

4 Summary

The group theoretical method given by Bhagavantam has been extended to derive the number of independent constants needed to describe optical activity in the 32 crystal classes

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PREPARATION OF PENTAMMINO CUPRIC SULPHATE FROM AMMONIACAL SOLUTIONS OF COPPER SULPHATE

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The study of the cupric-ammines has attracted the attention of a large number of workers, who have prepared and studied these compounds by various means. The existence of di-, tetra-, and penta-ammino compounds are well established In a recent communication Bhattacharya and Dey[1] have reported the existence of cupric hexammino-sulphate as well in ammoniacal solutions of copper sulphate and attempts for its isolation are being made

When an aqueous solution of ammonium hydroxide is added to a solution of cupric sulphate, cupric hydroxide precipitates first, which dissolves in excess of ammonia giving a deep blue liquid called eau celeste Numerous studies have been made on this liquid Immerwahr[2] has suggested that in solution the $Cu^{\cdot}$ ions get replaced by more complex cupric-ammino $Cu(NH_3)_n^{\cdot}$ ions Reychler[3] from freezing point measurements found that the complex ions behave more or less in the same way as the $Cu^{\cdot\cdot}$ ions. Konowaloff,[4] Gaus,[5] and Locke and Forssall[6] by absorption and vapour pressure experiments found the compound to be $Cu(NH_3)_4SO_4$ Dawson and McCrae[7] determined the distribution ratio between water and chloroform and found the Cu NH_3 ratio to be $1 \cdot 4$ Horn[8] supported the existence of the tetra-ammino compound and said that the Cu NH_3 ratio could never be greater than 1 : 4 This result is, however, definitely contradicted by the existence of the now well-known pentammino compound and of the hexammino compound as found by Dey and Bhattacharya In addition to the aforesaid workers, Blanchard[9] studied the blue liquid from viscosity data and Bouzat[10] from thermal data and obtained the evidence of the existence of cupric tetrammino sulphate in the solution. More recently Job[11] by absorption spectra studies determined the composition and found that it corresponded to that of the tetrammino compound Glasstone[12] by electrometric titration of copper sulphate with aqueous ammonia obtained evidence of the presence of $Cu(NH_3)_4^{\cdot\cdot}$ ions. Bhatnagar, Goyle and Prasad[13] however say that the blue colour of the cuprammino complex is due to copper-hydroxide in colloidal form.

Quite a number of methods are known for the isolation of the ammino-complexes from aqueous solution. Berzelius[14] recommended the addition of alcohol to an ammoniacal solution of copper sulphate when the compound separates out in pulverulent crystals. Bouzat[15] cooled a hot concentrated solution of the salt and quickly dried the crystals between filter-papers. Andre[16] prepared the salt by passing ammonia gas into a solution of copper sulphate. Horn and Taylor[17] and Dawson (*loc. cit.*) recommended this process. Pickering[18] obtained the compound by adding aqueous ammonia to an almost saturated solution of cupric sulphate until the precipitate of cupric hydroxide just redissolved and allowing the solution to stand for some time

The process of preparation in this study was that described by King[19] The compound precipitated by alcohol was decomposed by caustic soda solution and the precipitated copper oxide filtered and estimated. The expelled ammonia was passed into a standard acid solution and ammonia thus estimated The Cu : NH_3 ratio was found to be 1 · 5 thus suggesting the formula of the compound to be $Cu(NH_3)_5SO_4$, and not $Cu(NH_3)_4SO_4$ as reported by previous workers.

Experimental

10 Grams of finely powdered pentahydrated cupric sulphate (A R. quality) was dissolved in a mixture of 10 c.c water and 15 c.c Merck's ammonia solution (sp gr 0·888) To this well stirred blue solution were added 15 c c of alcohol from a dropping funnel The ammino compound separated out as a dark blue crystalline meal. This was filtered in a Buchner's funnel, washed thoroughly with alcohol and kept in a desiccator over lime

The ammonia present in the solid was determined by the Kjeldahl's distillation method and the copper was determined gravimetrically as copper oxide The following analytical values for the ratio of copper to ammonia were obtained:

Ratio		Total Analysis	
Cu NH_3		Found	Calculated
1 5·057	Copper .	25·04%	25·98%
1 4·993	Ammonia ..	34·64	34·78
1 4 986	Sulphate ..	39·01	39·36
1 5·053			
1 5·048		99·69	100·00

On estimation of sulphate, the ratio Cu SO_4 was found to be 1 1; water of crystallisation was found to be absent. It is evident that the compound obtained by us has the formula $Cu(NH_3)_5SO_4$

The pentammino compound as prepared by us smells of ammonia even at ordinary temperatures and it is evident that it slowly decomposes The surface layer of the salt gradually changes to bluish white even when the salt is preserved in a desiccator over lime The salt dissolves in water giving a deep blue solution, but hydrolyses on further addition of water and gives a precipitate of hydroxide When the deep blue solution is heated there is a brisk evolution of ammonia and a black deposit of cupric oxide is formed

Summary and Conclusion

The compound precipitated by the addition of alcohol to an ammoniacal solution of cupric sulphate was known to be cupric tetrammino sulphate. In this study this compound has been analysed and has been shown to be $Cu(NH_3)_5SO_4$

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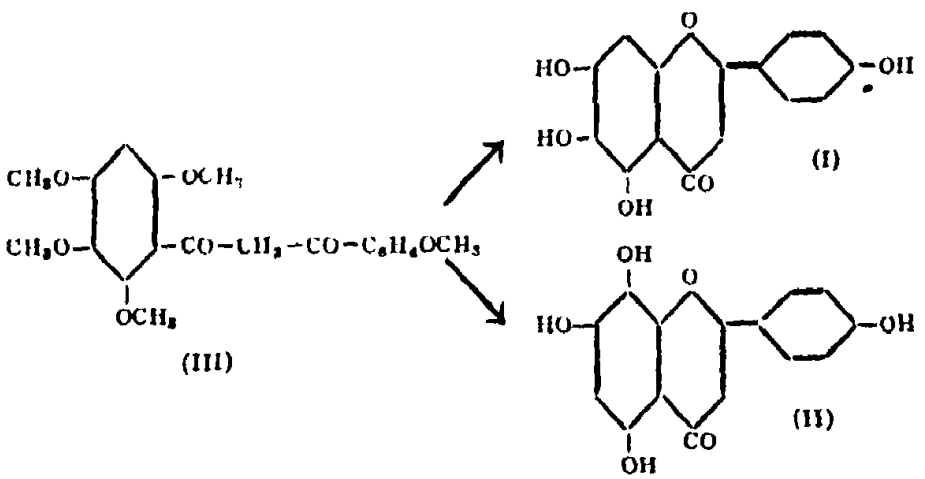
SYNTHESIS OF 5: 6: 7- HYDROXYFLAVONES AND THEIR DERIVATIVES—PART I

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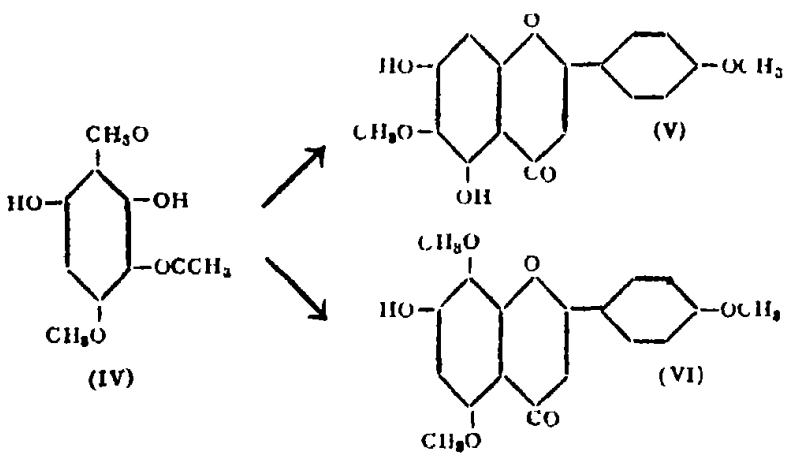
Of the possible flavones with the 5 6 7-arrangement of hydroxyls in the benzopyrone part only two are so far known to occur in nature either free or combined. They are baicalein and scutellarein The latter was the first to be discovered and studied It was isolated by Molisch and Goldschmiedt[1] from the leaves and flowers of *Scutellaria altissima*, it has also been found in the leaves and flowers of *S baicalensis* Its constitution was investigated by Goldschmiedt and Zerner[2] who concluded that it should be either 5:6:7:4'-(I) or 5 7 8.4'-tetrahydroxy flavone (II) This was confirmed by the synthesis of Bargellini[3] who submitted pentamethoxy-dibenzoylmethane (III) to the action of hydriodic acid The reaction could proceed in two ways, but actually scutellarein alone was obtained This synthesis, however, did not enable the choice to be made between the two alternatives



The trihydroxy flavone, baicalein was obtained from the roots of *S. baicalensis* by Shibata, Iwata and Nakamura[4] and it has also been found to be present in the root and stem barks of *Oroxylum indicum*[4] It resembles scutellarein closely in its properties The substance had already been synthesised by Bargellini[5] following the method adopted by him for scutellarein. Of the two possible isomers only one was again obtained

and that was given the 5 6, 7-constitution The main point mentioned in favour of this was that the product was not identical with hydroxy-chrysin obtained by Nierenstein[6] by the oxidation of chrysin and considered by him to be 5 : 7 · 8-trihydroxy flavone Since Nierenstein's claim was later shown to be wrong, this support lost its significance Hatton[7] who later repeated the above synthesis of Bargellini was not able to confirm the older observations regarding the exclusive formation of scutellarein from the diketone (III). Similar results were obtained by him even with regard to the baicalein synthesis Consequently the previous synthetic support for the constitution of these compounds could not be considered definite

Wessely and Moser[8] attempted to supply more definite evidence for the constitution of scutellarein by the synthesis of 5 7 8 · 4′-tetrahydroxy flavone in an unambiguous manner. For this purpose 2. 4-dihydroxy-3. 6-dimethoxy acetophenone (IV) was heated with the anhydride and sodium salt of anisic acid according to the method of Allan and Robinson The product was, however, found to be a dimethyl ether of scutellarein (V) and this extraordinary result was attributed to initial demethylation in the ortho-position of the ketonic group and subsequent ring closure favouring the 5. 6 · 7-arrangement Thus even in this method complications were found to exist In one of the large number of experiments, however, such demethylation did not occur and the normal condensation product, 7-hydroxy-5. 8 · 4′-trimethoxy flavone (VI) was produced

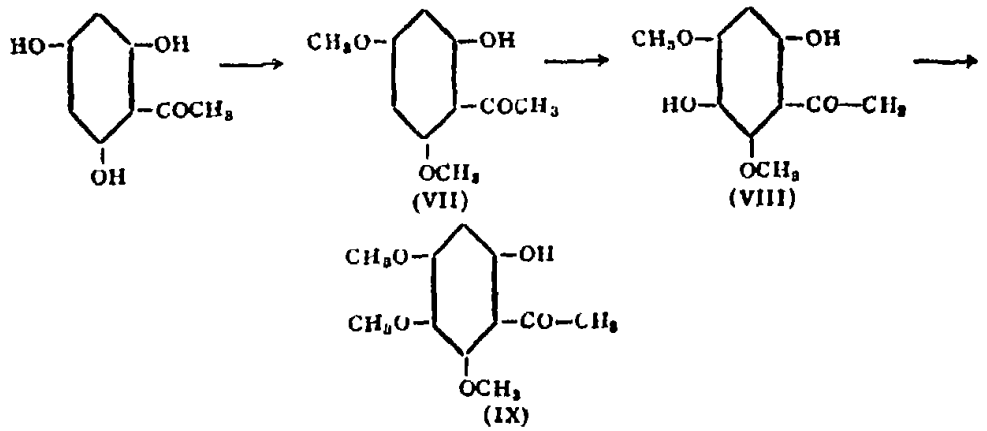


An unequivocal proof for the constitution of scutellarein was provided by Robinson and Schwarzenbach[9] who synthesised its tetramethyl ether by a novel method in which the 4-aminoderivative of the corresponding flavylium salt was an intermediate This method, however, involves the preparation of

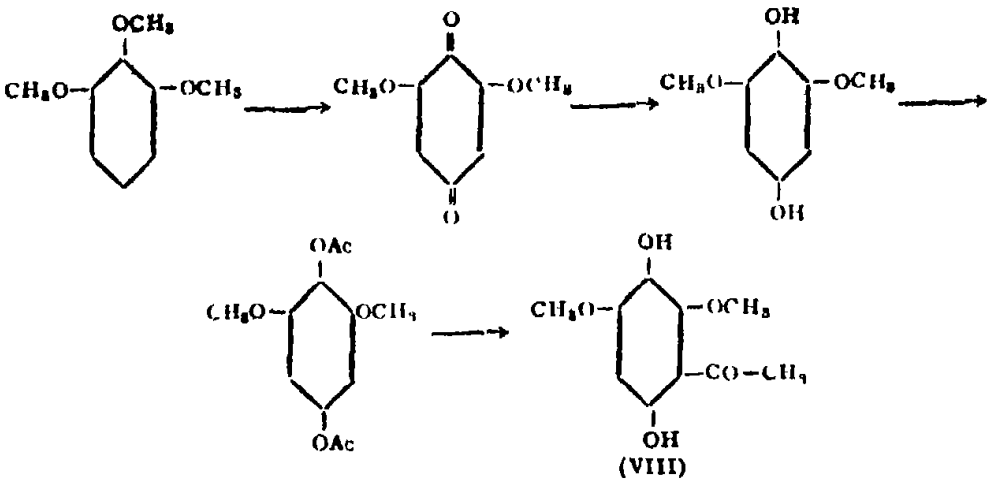
aroyl-pyruvamides which are not easily accessible and hence has not been generally employed for the synthesis of flavones

In view of the position reviewed above, a simple and at the same time unambiguous method of synthesis of the 5:6:7-hydroxyflavones seemed to be needed One such method which will also be useful for the study of the partial methyl ethers of baicalein and scutellarein has now been worked out The required ortho-hydroxy ketone has been prepared by an unambiguous method and converted into the flavones by adopting the Baker-Venkataraman[10] procedure which is free from complications. The constitution of the products are therefore free from doubt and the work reported in this paper therefore provides unequivocal confirmation of the constitutions of baicalein and scutellarein

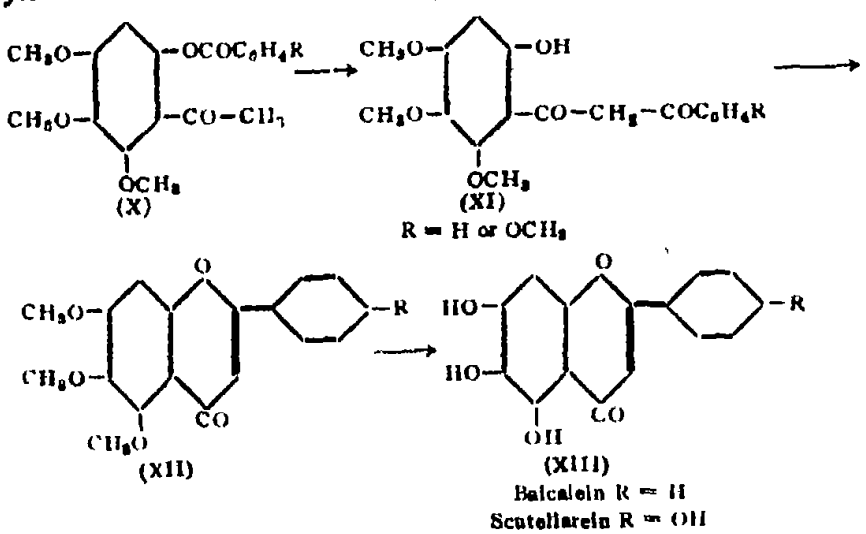
2-Hydroxy-4 5·6-trimethoxyacetophenone (IX) has now been prepared starting from phloroacetophenone and passing through the stages indicated below Phloroacetophenone is subjected to partial methylation using the requisite amounts of dimethyl sulphate and potassium carbonate The 4:6-dimethyl ether (VII) is obtained in good yield. This compound was originally made by Kostanecki and Tambor[11] by the partial demethylation of phloroacetophenone trimethyl ether and was subsequently obtained by Canter, Curd and Robertson[12] along with the *p*-hydroxy isomer by the Hoesch condensation of phloroglucinol dimethyl ether with acetonitrile



Phloroacetophenone-dimethyl ether (VII) undergoes smooth oxidation with potassium persulphate in alkaline solution to give the 2:5-dihydroxy compound (VIII) in good yield. The constitution of this ketone is arrived at not only from analogy with a large number of similar cases[13], but is supported by its reactions. This compound was obtained earlier by Mauthner[14] starting from pyrogallol trimethyl ether and proceeding as indicated below:



The new method of preparation seems to be definitely better The final stage is partial methylation converting the dihydroxy ketone (VIII) into (IX).[12] Its benzoyl and anisoyl derivatives (X) undergo rearrangement into the ortho-hydroxy diketones (XI) in the presence of sodamide in toluene solution and ring closure to the flavones (XII) is effected by heating with glacial acetic acid and sodium acetate. Demethylation with boiling hydriodic acid yields baicalein and scutellarein (XIII)



The hydroxy compounds and the methyl ethers have all the properties recorded for baicalein, scutellarein and their derivatives. The synthetic baicalein and its derivatives have been compared with samples obtained from *Oroxylum indicum* and found to be identical The following important

points may be noted. Neither the hydroxy flavone nor their methyl ethers develop any fluorescence in alcoholic or concentrated sulphuric acid solution The two hydroxy compounds resemble each other in their reaction with alcoholic ferric chloride, lead acetate and sodium amalgam and differ in their behaviour with sodium hydroxide. While baicalein yields rapidly bluish-green flocks on the addition of aqueous alkali, scutellarein dissolves to give a greenish yellow solution which rapidly turns deep green.

Experimental

2-Hydroxy-4 6-dimethoxyacetophenone (VII).—Phloracetophenone (4 2 g) dried in an air-oven at 120°, was dissolved in dry acetone (15 c c.), to the clear solution was added dry benzene (75 c c), freshly ignited potassium carbonate (15 g) and dimethyl sulphate (6·5 g., 2 2 mols) and the mixture refluxed on the water-bath for 12 hours with occasional shaking The inorganic salts were then filtered and washed with hot benzene The filtrate was washed twice with water, (20 c c) each time, and then extracted with 5% aqueous sodium hydroxide four times. The united alkaline extract was poured into ice-cold dilute hydrochloric acid when 2-hydroxy-4 6-dimethoxy acetophenone was precipitated as a practically colourless crystalline mass It was filtered and thoroughly macerated with 5% aqueous sodium carbonate to remove any monomethyl ether that might have been formed, and again filtered and washed well with water (The filtrate did not yield any crystalline solid on acidification) Yield, 3·2 g On crystallisation from dilute alcohol it was obtained as colourless irregular prisms melting at 82-83° (Canter, Curd and Robertson[10] give m.p 81–82°) It dissolved in aqueous alkali to an yellow solution and gave a brownish-red ferric reaction in alcoholic solution

The substance (0 5 g) was acetylated by heating with acetic anhydride (5 c c) and freshly fused sodium acetate (1 0 g) on the boiling water-bath for two hours The acetyl derivative crystallised from ethyl acetate as stout rhombic prisms and melted at 106-107° (Canter, Curd and Robertson[18] give m p 106–7°)

2 . 5-Dihydroxy-4 6-dimethoxy-acetophenone (VIII) —2-Hydroxy-4 6-dimethoxy-acetophenone (15 g) was dissolved in aqueous sodium hydroxide (20 g in 200 c c of water), the solution cooled to a temperature of 15–20° and kept continuously stirred. A solution of potassium persulphate (22 g.; 1·1 mol.) in water (300 c.c.) was then introduced dropwise during the course of 4 hours, the temperature being maintained at 15–20° throughout the reaction. After allowing to stand for 24 hours, the dark reddish-brown

reaction mixture was rendered distinctly acid to litmus by the addition of concentrated hydrochloric acid The unreacted original ketone which was precipitated as a dark brown crystalline solid, was filtered and washed with a small quantity of water. The clear aqueous filtrate was treated with sodium sulphite (5 g) and animal charcoal (3 g) and again filtered after stirring well for about 5–10 minutes. Concentrated hydrochloric acid (150 c.c) was then added and the solution heated on the boiling water-bath for ½ hour. On cooling it rapidly deposited a brownish yellow crystalline mass which was collected, and washed with water Yield, 5 g The filtrate was twice extracted with ether and the solvent distilled when a further quantity (1 g.) of the dihydroxy-compound was obtained If the solution should be heated on the water-bath for a longer duration (1 hour) for the hydrolysis, the product obtained was very deep brown in colour and was difficult to purify. When twice crystallised from aqueous alcohol using animal charcoal the substance was obtained as stout yellow rhombic prisms melting at 164–65° (Mauthner[14] gives m.p 162–63°) It was moderately soluble in hot water, more so in alcohol and acetone, but sparingly soluble in light petroleum Its solution in aqueous sodium hydroxide was bright yellow and turned deep reddish-brown on keeping. In alcoholic solution the substance gave a transient green colouration with ferric chloride which rapidly became reddish-brown either on keeping or on the addition of a slight excess of the reagent. No precipitate was obtained with lead acetate in alcoholic solution. (Found: C, 56·8; H, 5 4, $C_{10}H_{12}O_5$ requires C, 56·6; H, 5 7%)

2 · 5-*Dibenzoyloxy*-4 · 6-*dimethoxy acetophenone*—Dry pyridine (8 c c) and benzoyl chloride (1·5 g) were added to the above *p*-dihydroxy acetophenone (1 0 g) and the mixture heated on the boiling water-bath for 20 minutes. It was added to ice-cold water containing a few c c of hydrochloric acid and the precipitated brown solid collected, washed with water and crystallised twice from alcohol in which it was moderately soluble The dibenzoate was thus obtained as colourless thick aggregates of micaceous plates and it melted at 153–54°. The substance did not dissolve in cold aqueous alkali and gave no colour with ferric chloride in alcoholic solution (Found: C, 68·4, H, 5 1; $C_{24}H_{20}O_7$ requires C, 68 6; H, 4 8%)

2-*Hydroxy*-4 : 5 : 6-*trimethoxy acetophenone* (IX).—The 2 · 5-dihydroxy-compound (2 g) was dissolved in a mixture of dry acetone (10 c c) and dry benzene (75 c.c.) and to this solution were added acid-free dimethyl sulphate (1 c.c.; 1·1 mol) and freshly ignited potassium carbonate (6 g.). The mixture was heated under reflux for 12 hours, the inorganic salts filtered and washed with a small quantity of hot benzene The benzene filtrate was

washed with 5% aqueous sodium carbonate in order to remove any unmethylated dihydroxy-compound and then extracted with 10% aqueous sodium hydroxide. The united alkaline extracts were acidified with ice-cold (1 : 1) hydrochloric acid when the partially methylated ether was obtained as a reddish-brown oil. It was taken in ether, the ether solution dried over sodium sulphate and the solvent distilled The residue was then treated with light petroleum (b p 40-60°) when the last traces of unchanged dihydroxy compound were precipitated After allowing to stand for an hour, the petroleum ether solution was carefully decanted and the solvent was distilled off; 2-hydroxy-4 : 5 · 6-trimethoxy acetophenone was left behind as an yellow oil Yield, 1·5 g It dissolved in aqueous sodium hydroxide to an yellow solution and gave a deep violet brown colour with ferric chloride in alcoholic solution (*cf* Baker[18])

2-*Benzoyloxy*-4 5 6-*trimethoxy acetophenone* (*X*, *R* = *H*)—The above compound (2 g) was dissolved in dry pyridine (10 c c) and treated with benzoyl chloride (1 5 c c) After shaking well for five minutes, the mixture was heated on the water-bath for ½ hour and then added to ice-water containing hydrochloric acid. The benzoyl derivative which separated as an oil was taken in ether, the ether solution washed successively with dilute hydrochloric acid, and aqueous sodium hydroxide After a final washing with water, the solution was dried over calcium chloride and the solvent distilled The solid product was crystallised first from alcohol, then from benzene and finally from benzene-alcohol mixture The benzoyl derivative was thus obtained as broad rectangular plates and prisms and melted at 87–88°. Yield, 2 g The substance gave no ferric reaction and did not dissolve in cold aqueous alkali (Found: C, 65 6, H, 5·8, $C_{18}H_{18}O_6$ requires C, 65·5, H, 5 5%)

2-*Hydroxy*-4 : 5 6-*trimethoxydibenzoylmethane* (*XI*, *R* = *H*)—To a solution of the above benzoyl derivative (2 g.) in dry toluene (30 c c) was added sodamide (8 g) which had been finely powdered under toluene. The mixture was well stirred for 10 minutes and then heated on the boiling water-bath for 4 hours with frequent shaking. The yellow solid product was filtered, washed well with hot benzene, dried and carefully added to ice-cold water. The resulting yellow solution was filtered and saturated with carbon dioxide The dibenzoylmethane separated as a deep orange-red oil which turned into a deep-yellow solid when left in the refrigerator for two days. It was collected, washed with water, dried and crystallised from benzene, light petroleum mixture; Yield, 1 2 g. After a second crystallisation from the same solvent the diketone was obtained as golden yellow rectangular

plates and prisms and melted at 99–100°. It was easily soluble in alcohol, acetone and benzene and dissolved in aqueous sodium hydroxide to a bright yellow solution. Its alcoholic solution gave a deep brownish-green colour with ferric chloride. (Found: C, 65 3; H, 5 8, $C_{18}H_{16}O_6$ requires C, 65 5; H, 5·5%)

5·6·7-*Trimethoxy-flavone* (*Baicalein trimethyl ether, XII, R = H*).—The dibenzoylmethane (1 g) was dissolved in glacial acetic acid (10 c c.) and to the solution was added fused sodium acetate (2 g). The mixture was gently boiled over a wire-gauze for 4 hours and then diluted with water (100 c c) When allowed to stand for two or three hours, the solution deposited a practically colourless crystalline solid which was collected, washed, and crystallised from aqueous alcohol Yield, 0·6 g On recrystallisation from dilute alcohol the trimethoxyflavone was obtained as colourless elongated rectangular prisms (mostly rods) and melted at 165–66° (Hattori[3] gives m.p. 163–64°) It was insoluble in aqueous sodium hydroxide and gave no colour with ferric chloride. Its solution in concentrated sulphuric acid was yellow without any fluorescence in daylight. With magnesium and concentrated hydrochloric acid its alcoholic solution developed an orange-yellow colour. (Found C, 69 1; H, 4·9, $C_{18}H_{16}O_5$ requires C, 69 2, H, 5 1%)

5:6 7-*Trihydroxy-flavone* (*Baicalein, XIII, R = H*)—The foregoing methoxy flavone (0 3 g.) was dissolved in acetic anhydride (5 c.c.) and cautiously treated with hydriodic acid (*d.* 1·7; 5 c c.) and the mixture heated at 135–40° for two hours (oil-bath). On pouring the cooled reaction mixture into water saturated with sulphur dioxide, the trihydroxy flavone separated as an yellow solid, which was collected, boiled with water and crystallised twice from alcohol. It formed yellow coloured narrow rectangular plates and melted at 264–65° (Shibata, Iwata and Nakamura[4] give m.p. 264–65°).

The trihydroxy flavone was moderately soluble in alcohol, more so in acetone and glacial acetic acid, but sparingly soluble in petroleum ether. Its solution in concentrated sulphuric acid was deep yellow and exhibited no fluorescence. In alcoholic solution it gave an orange-yellow precipitate with lead acetate, and a brown colour with a tinge of green with ferric chloride. When added to aqueous ammonia, the crystals developed an orange-red colour and dissolved to give a bright-yellow solution. The flavone dissolved with difficulty in aqueous sodium carbonate to a greenish-yellow solution which gave a dark greenish-brown precipitate on keeping. In 10% aqueous sodium hydroxide the crystals turned deep red in colour and subsequently changed into greenish-brown flocks. When treated with

sodium amalgam in absolute alcohol, it immediately gave green flocks (Bargellini's test). (Found: C, 66·6, H, 4·0; $C_{16}H_{10}O_5$ requires C, 66·7; H, 3·7%.)

Baicalein triacetate.—The triacetate was prepared by treating the flavone (0·1 g.) with acetic anhydride (5 c.c.) and fused sodium acetate (1 g.) and boiling the mixture for two hours. When crystallised twice from ethyl acetate, it was obtained as short, colourless rectangular rods and it melted at 194–95° with slight sintering at 190° (Shibata, Iwata and Nakamura[4] give m.p. 191–92°).

2-*Anisoyloxy*-4·5·6-*trimethoxyacetophenone* (*X*, $R = OCH_3$).—2-Hydroxy-4·5:6-trimethoxyacetophenone (IX) (2 g.) was anisoylated by heating with anisoyl chloride (2 c.c.) and dry pyridine (10 c.c.), for ½ hour on the boiling water-bath and the product worked up as in the case of the benzoyl derivative. The colourless crystalline solid, obtained on removal of the ether, was crystallised from alcohol, benzene and finally from benzene-light petroleum mixture. The anisate was thus obtained as (colourless) stout prisms and it melted at 112–13°. It did not dissolve in cold aqueous sodium hydroxide and gave no ferric reaction. (Found: C, 63·3; H, 5·2; $C_{19}H_{20}O_7$ requires C, 63·3, H, 5·6%.)

2-*Hydroxy*-4·5:6:4′-*tetramethoxydibenzoylmethane* (*XI*, $R = OCH_3$).—A solution of the above *O*-anisoyl derivative (2 g.) in dry toluene (30 c.c.) was treated with finely powdered sodamide (8 g.). The mixture which rapidly turned yellow was heated on the boiling water-bath for 5 hours and the yellow solid collected, washed with hot benzene, dried and added to ice-water. The yellow solution was saturated with carbon dioxide and the dibenzoylmethane which first separated as an oil, solidified on leaving in the refrigerator for two days. The solid was then collected, dried and crystallised from benzene-light petroleum mixture when it was obtained as bright yellow rectangular prisms melting at 114–15°. Yield, 1·2 g. It was readily soluble in alcohol, acetone and benzene but less so in petroleum ether. It dissolved in aqueous alkali to give a bright yellow solution and gave an olive green colour with ferric chloride in alcoholic solution. (Found: C, 63·5; H, 5·9; $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%.)

5·6·7·4′-*Tetramethoxy flavone* (*Scutellarein tetramethyl ether*) (*XII*, $R = OCH_3$).—A mixture of the above dibenzoylmethane (1 g.), glacial acetic acid (10 c.c.) and fused sodium acetate (2 g.) was gently boiled for 4 hours and diluted with water (100 c.c.). The aqueous solution was extracted with ether and the ether solution carefully shaken with 5% aqueous sodium carbonate to remove acetic acid and then washed with water. On

distillating off the solvent, a colourless crystalline solid was obtained which was recrystallised from dilute alcohol. Yield, 0·8 g It was readily soluble in the common organic solvents and on recrystallisation from aqueous alcohol, scutellarein tetramethylether was obtained as colourless stout cubical crystals and melted at 162–63° (Goldschmiedt and Zerner[3] give m.p 158-60°). It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcoholic solution. It dissolved in concentrated sulphuric acid to give an yellow solution which exhibited no fluorescence. (Found in a sample dried *in vacuo* at 130° for two hours; C, 66 8; H, 5 5, $C_{19}H_{18}O_8$ requires C, 66 7, H, 5·3%)

5.6:7·4'-*Tetra-hydroxy flavone* (*Scutellarein, XIII, R = OH*).—The demethylation of the tetramethoxy flavone (0 2 g.) was effected by heating (oil-bath) at 135–40° with acetic anhydride (5 c c) and hydriodic acid (*d*, 1 7; 5 c c) The tetrahydroxy flavone was twice crystallised from alcohol when it was obtained as short, yellow needles Yield, 0 15 g It turned brown at about 300° and did not melt down below 340° (Goldschmiedt and Zerner[3] found that it becomes dark at about 300° and does not melt or decompose below 330°). The substance dissolved in alcohol, acetone and ethyl acetate with difficulty but more readily in glacial acetic acid Its solution in concentrated sulphuric acid was yellow without any fluorescence With lead acetate in alcoholic solution it gave an orange yellow precipitate and with ferric chloride it developed a green colour which turned brown with a tinge of green The substance dissolved in ammonia to give a bright yellow solution which subsequntly turned orange-brown; in aqueous sodium carbonate it gave an yellow colour which rapidly turned green In aqueous sodium hydroxide it formed a deep greenish-yellow solution which immediately became pure green in colour, no precipitate was obtained even on keeping the solution for 24 hours When the substance was treated with sodium amalgam in absolute alcohol, there was an immediate formation of green flocks (Bargellini's test) (Found· C, 63 0; H, 3 8, $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%)

Scutellarein tetraacetate.—The tetraacetate prepared by heating (oil-bath) the hydroxy flavone (0·1 g) with acetic anhydride (5 c c) and fused sodium acetate (1 g) was crystallised twice from acetic acid-alcohol mixture It was obtained as long fine needles and melted at 240–41° (Goldschmiedt and Zerner[3] give m p. 235–37°, Wessely and Moser[8] give m p 238°)

Summary

A simple and at the same time unambiguous method of synthesis of the 5:6:7-hydroxyflavones, baicalein and scutellarein and their derivatives is

described. It starts from phloracetophenone which is partially methylated to the 4.6-dimethyl ether. Oxidation of this ether with potassium persulphate yields the 2:5-dihydroxy compound which on partial methylation produces 2-hydroxy-4:5.6-trimethoxyacetophenone. Using the benzoyl and anisoyl derivatives of this ketone and adopting the Baker-Venkataraman procedure, the trimethyl ether of baicalein and the tetramethyl ether of scutellarein have been prepared and from them the hydroxyflavones and their acetates.

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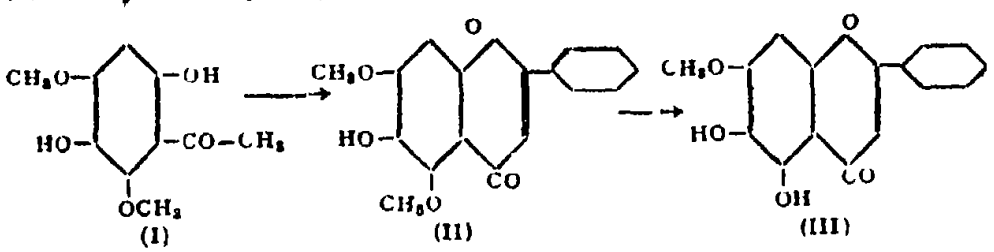
SYNTHESIS OF 5:6:7-HYDROXYFLAVONES AND THEIR DERIVATIVES—PART II

By V. D Nageswara Sastri and T R. Seshadri

(From the Department of Chemistry, Andhra University)

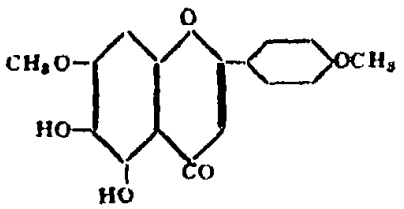
Received February 26, 1946

In continuation of the work described in Part I,[1] an attempt has been made to prepare partially methylated derivatives of baicalein and scutellarein For this purpose 2:5-dihydroxy-4:6-dimethoxy acetophenone (I) is subjected to the Allan-Robinson condensation using the anhydride and sodium salt of (1) benzoic acid and of (2) anisic acid. In the first case the product is 5 7-dimethoxy-6-hydroxyflavone (II) On methylation it yields 5.6.7-trimethoxy flavone, baicalein-trimethyl ether, identical with the sample prepared by the Baker-Venkataraman method [1] Partial demethylation could be effected using aluminium chloride under mild conditions yielding 7-methoxy-5.6-dihydroxyflavone (baicalein-7-methyl ether III)

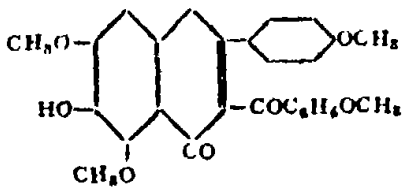


In its properties and reactions it is markedly different from oroxylin-A[2] which is considered to be the 6-methyl ether of baicalein The mixed melting point with a sample of the latter obtained from the root bark of *Oroxylum indicum* is depressed. The comparison is brought out in the following table.

	Oroxylin-A	7-Methyl ether of Baicalein
Appearance .	Yellow needles	Thick rhombohedral prisms (Yellow)
M.p. of the substance ..	230–31°	219–20°
,, acetate .	131–32°	239–40°
Alcoholic $FeCl_3$ ..	Red-violet	Green
Aq. NaOH ..	Yellow solution	Greenish brown precipitate
Na Amalgam .	Yellow solution	Blue solution, and a brown precipitate after an interval



(IV)



(V)

The condensation of the above dihydroxy ketone (I) with anisic anhydride and sodium anisate gives rise to two products which could be separated by fractional crystallisation from alcohol The less soluble component is a dimethyl ether whose colour reactions are very similar to those of the 7-methyl ether of baicalein. On methylation it yields the tetra-methyl ether of scutellarein and hence it is considered to be the 7 4'-dimethyl ether of scutellarein (IV) Its formation should be due to partial demethylation taking place during the Allan-Robinson condensation Such demethylation has been noted in many other similar cases

The second product obtained in very poor yields resembles in its reactions 5: 7-dimethoxy-6-hydroxyflavone (II). Its methyl ether is, however, different from scutellarein tetramethyl ether. Hence it is not 5 7. 4'-tetramethoxy-6-hydroxyflavone The analytical results agree with the requirements for the 3-anisoyl derivative (V)

The above mentioned 7 4'-dimethyl ether of scutellarein is different in its properties from the isomeric 6. 4'-dimethyl ether prepared by Wessely and Moser[3] and considered to be identical with the dimethyl ether occurring in the flowers of *Linaria vulgaris*[4] The differences are shown below.

	7 4'-dimethyl ether of scutellarein	6 4'-dimethyl ether
Appearance	Yellow rectangular plates	Fine yellow needles
Melting point	211–12°	201°, 210°
Aq. NaOH	Slowly forms a greenish yellow solution and a greenish brown precipitate is deposited	Yellow solution
$FeCl_3$ reaction	Stable green	Dark brown

Experimental

5 · 7-Dimethoxy-6-hydroxyflavone (II) —2. 5-Dihydroxy-4: 6-dimethoxyacetophenone (1 g.), benzoic anhydride (5 g) and sodium benzoate (2 g) were intimately mixed and heated under diminished pressure at 180–85° (oil-bath) for 4 hours After cooling, the hard brown mass was broken up, alcohol (50 c c) added and the mixture refluxed on the water-bath for 10

minutes. A solution of potassium hydroxide (4 g) in water (6 c c) was then gradually introduced during the course of 15 minutes and the refluxing continued for a further 20 minutes After distilling the alcohol under reduced pressure, the greenish-brown residue was dissolved in water (100 c.c.) and the solution filtered to remove any insoluble matter. On saturating it with carbon dioxide, the crude flavone separated as a brown solid which was filtered and crystallised twice from alcohol (animal charcoal) Yield 0 2 g By another crystallisation from the same solvent, the dimethoxyflavone was obtained as pale yellow thick cubical crystals whereas it came down as fine needles when quickly crystallised It melted at 212–13° and a further crystallisation did not raise the melting point.

It was moderately soluble in alcohol and more easily in acetone and glacial acetic acid It dissolved in aqueous sodium hydroxide to give a bright a yellow solution In alcoholic solution it gave a weak brown colouration with ferric chloride and its solution in concentrated sulphuric acid was yellow without any fluorescence in daylight (Found· C, 68 6; H, 4·9; $C_{17}H_{14}O_5$ requires C, 68 5, H, 4 7%)

The substance (0 1 g) was acetylated by refluxing (oil-bath) with acetic anhydride (5 c c) and fused sodium acetate (1 g.) for 3 hours. The acetate was crystallised from dilute acetic acid when it was obtained as colourless stout plates melting at 218-19° It did not dissolve in cold aqueous alkali and gave no ferric reaction (Found C, 66 9; H, 4·9; $C_{19}H_{16}O_6$ requires C, 67·1, H, 4 7%)

5, 6, 7-*Trimethoxyflavone* (*Baicalein trimethyl ether*)—The dimethoxy flavone (0·15 g) was methylated in dry acetone (25 c c) using anhydrous potassium carbonate (2 g) and dimethyl sulphate (1 c.c) and boiling for 12 hours The crude methyl ether separated as a practically colourless crystalline solid and it crystallised from dilute alcohol as colourless elongated rectangular prisms, melting at 165-66° It was identical with baicalein trimethyl ether already reported[1] and the mixed melting point was undepressed. (Found· C, 68·9; H, 5·4; $C_{18}H_{16}O_5$ requires C, 69 2 H, 5·1%.)

7-Methoxy-5· O-dihydroxyflavone (*7-O-methyl baicalein*)—The partial demethylation of the above dimethyl ether (II) had to be effected under carefully controlled conditions Excess of aluminium chloride and high temperature resulted in the reaction going too far producing baicalein.

To a solution of the dimethoxyflavone (0·25 g) in nitrobenzene (25 c.c.) was added finely powdered anhydrous aluminium chloride (0·5 g.) and the mixture kept at the laboratory temperature for 24 hours. On the addition of petroleum ether, a yellow solid was precipitated, which was collected and

washed with a further quantity of petroleum ether to remove adhering nitrobenzene The solid was added to water (50 c c) containing concentrated hydrochloric acid (2 c.c) and glacial acetic acid (5 c.c.) and the mixture heated on the boiling water-bath for 15 minutes The solution was then cooled and further diluted with water when the 7-methyl ether separated as an yellow crystalline solid It was filtered, washed and crystallised twice from alcohol. Yield 0·15 g. On recrystallisation from absolute alcohol, it was obtained as thick rhombohedral prisms and melted at 219–20°. The melting point was depressed on admixture with an equal quantity of oroxylin-A The dihydroxyflavone was moderately soluble in alcohol and acetone, and gave a stable green colouration with ferric chloride in alcoholic solution With aqueous sodium hydroxide the crystals developed an orange-red colour and then changed into a dark greenish-brown precipitate On treatment with sodium amalgum in absolute alcohol (Bargellini's test), the dihydroxyflavone gave an orange yellow solution which rapidly changed through green to blue in colour; a brown precipitate was obtained after some time With lead acetate in alcoholic solution it gave an orange yellow precipitate The yellow solution in concentrated sulphuric acid exhibited no fluorescence. (Found: C, 67·5; H, 4·4; OCH_3, 10 3; $C_{16}H_{12}O_5$ requires C, 67 6; H, 4 3, OCH_3, 10 9%)

The dihydroxyflavone (0·1 g) was acetylated by refluxing (oil-bath) with acetic anhydride (5 c c.) and sodium acetate (1 g.) for two hours The diacetate was crystallised twice from ethyl acetate when it was obtained as shining elongated hexagonal plates melting at 239–40° (Found: C, 65 1, H, 4 6; $C_{20}H_{16}O_7$ requires C, 65 2, H, 4·3%)

5:6-*Dihydroxy*-7: 4'-*dimethoxyflavone* (7.4'-*O*-*dimethyl scutellarein*) — An intimate mixture of the dihydroxyacetophenone (I, 2 g.), anisic anhydride (12 g.) and sodium anisate (4 g) was heated under diminished pressure at 180–85° (oil-bath) for 6 hours The hydrolysis was effected by refluxing with alcohol (100 c.c.) and a solution of potassium hydroxide (10 g.) in water (10 c.c.) and the product worked up in the usual manner. The crude product obtained on saturating the alkaline solution with carbon dioxide was filtered and washed with water. Yield, 0·25 g It gave two fractions on crystallisation from alcohol. When the hot alcoholic solution was cooled, a sparingly soluble yellow solid first separated. It was collected and crystallised twice from the same solvent when 5:6-dihydroxy-7:4'-dimethoxyflavone was obtained as yellow rectangular plates, melting at 211–13° with sintering at 208°. Yield, 0·15 g. Further crystallisation did not raise the melting point. The substance was moderately soluble in acetone but not so

readily in alcohol Its solution in concentrated sulphuric acid was yellow and exhibited no fluorescence. In alcoholic solution it gave a stable green colouration with ferric chloride. When treated with dilute aqueous sodium hydroxide, the substance first became orange-red, then turned into greenish-blue flakes and dissolved to give a greenish-yellow solution; on allowing to stand, a greenish-brown precipitate was subsequently deposited. (Found: C, 65·0; H, 4·7; OCH_3, 19 0, $C_{17}H_{14}O_6$ requires C, 65·0, H, 4 5; OCH_3, 19·7%.)

The dihydroxyflavone (0 1 g) was methylated using dry acetone (30 c c.), anhydrous potassium carbonate (1 g) and acid-free dimethyl sulphate (0·5 c.c.) The methyl ether was crystallised from dilute alcohol when it was obtained as colourless stout cubical crystals melting at 161-62° and identical with scutellarein tetramethyl ether

5, 7 : 4'-*trimethoxy*-6-*hydroxy*-3-*anisoyl-flavone* — The alcoholic mother-liquor obtained after filtering off the above compound, was concentrated and allowed to cool A pale greenish-yellow solid separated which after two crystallisations from dilute alcohol came out as pale yellow narrow rectangular plates and melted at 224-26° Yield, 75 mg It dissolved in aqueous sodium hydroxide to give an yellow solution Its solution in alcohol gave a weak brown colouration with ferric chloride (Found: C, 67·7; H, 4 9; OCH_3, 26 4, $C_{26}H_{22}O_8$ requires C, 67 5, H, 4 7; OCH_3, 26·8%)

Summary

Employing 2 : 5-dihydroxy-4 6-dimethoxyacetophenone and the Allan-Robinson method, the 5 : 7-dimethyl ether of baicalein is obtained and from it by partial demethylation the 7-methyl ether. This is definitely different from oroxylin-A, The use of anisic anhydride in the above condensation yields two products, (1) 7 : 4'-dimethyl ether of scutellarein and (2) 5 : 7 : 4'-trimethyl ether of 3-anisoyl-scutellarein The former is different from the 6 : 4'-dimethyl ether obtained from natural sources.

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SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

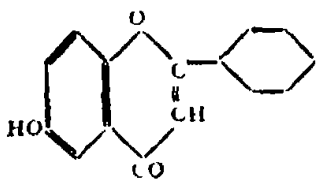
Part XX. A New Synthesis of 5 6 Dihydroxyflavone

By R N. Iyer and K. Venkataraman

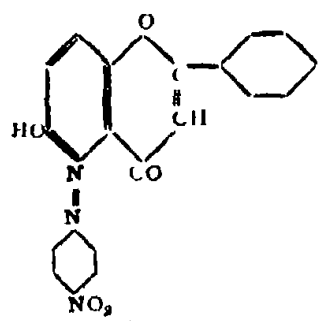
(From the Department of Chemical Technology, University of Bombay)

Received April 23, 1946

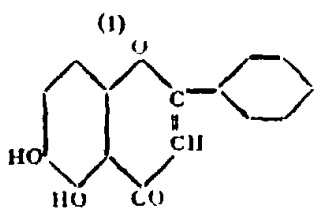
Examining the reactivity of natural colouring matters derived from phloroglucinol towards diazo salts, A G Perkin[1] found that chrysin, apigenin, euxanthone and catechin gave *di*azo dyes Mahal and one of us[2] have shown that 6-hydroxyflavone (I) couples with diazotised *p*-nitraniline to form a mono-azo dye, formulated as (II) in view of the stabilisation of one of the Kekule forms of the benzene ring in chromone due to fusion with the γ-pyrone ring, as indicated in (I) It was suggested[2, 3] that a route to the synthesis of 5. 6-dihydroxyflavone (III) thus becomes possible. We have now confirmed that 6-hydroxyflavone couples with diazo salts in the 5-position, and have synthesised 5: 6-dihydroxyflavone by a method which promises to be of value for the synthesis of other di- and polyhydroxyflavones and flavonols



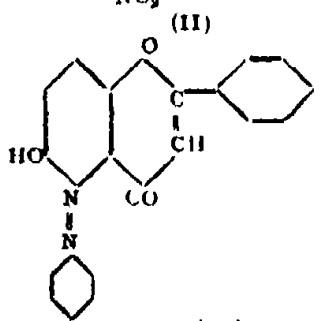
(I)



(II)

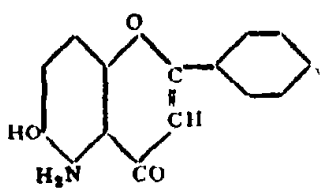


(III)

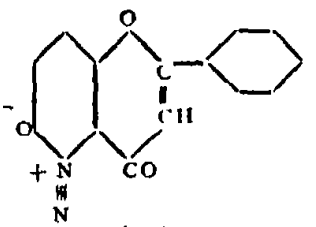


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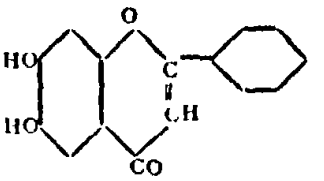
Coupling diazobenzene chloride with 6-hydroxyflavone (I), dissolved in alcohol-pyridine with the addition of ammonia, a nearly quantitative yield of 5-benzeneazo-6-hydroxyflavone (IV) was obtained 6-Hydroxyflavone is sparingly soluble in aqueous caustic soda, and the sodium salt tends to separate at the low temperature necessary for coupling, although diazotised *p*-nitraniline on account of its greater coupling energy in comparison with diazobenzene chloride couples readily with the flavone even under these conditions. The dye (IV) was reduced to 5-amino-6-hydroxyflavone (V) by means of zinc dust in boiling acetic acid. Other reagents for this reduction, as well as the hydrosulphite reduction of the alkali-soluble azo dye obtained by coupling diazotised sulphanilic acid with 6-hydroxy-



(V)



(VI)



(VII)

flavone, were tried, but various difficulties were encountered in the isolation of the aminohydroxyflavone; and the zinc-acetic acid procedure was found to be the most suitable

When the amine (V) was dissolved in hydrochloric acid and treated with sodium nitrite, the brownish yellow product crystallised from alcohol in needles, which were insoluble in aqueous alkali, gave a yellow solution in concentrated sulphuric acid, gave no colouration with ferric chloride and decomposed on heating at about 173° From these reactions and the nitrogen content, the substance is regarded as the diazo oxide (VI).[4] Boiled with 50% sulphuric acid, the diazo oxide (VI) underwent hydrolysis, and gave a dihydroxyflavone, which agreed in all its properties, including the m.p of the diacetyl derivative, with the 5:6- (III), and not with the 6:7-isomer (VII) 6:7-Dihydroxyflavone (VII) has been synthesised by Chadha and one of us[5] by the Robinson reaction on 2 4:5-trihydroxyacetophenone; and 5:6-dihydroxyflavone by Baker[6] by the action of sodamide[7] on 2-benzoyloxy-5·6-dimethoxyacetophenone, followed by cyclicisation and demethylation. Nakazawa[8] has synthesised 5:6-dihydroxyflavone by a route very similar to Baker's; 2-hydroxy-6-methoxyacetophenone was oxidised to 2:5-dihydroxy-6-methoxyacetophenone, the dibenzoate of which was converted to the β-diketone by the sodamide method[7]; cyclicisation and hydrolysis gave 5-methoxy-6-hydroxyflavone, which was demethylated[9] by means of aluminium chloride in nitrobenzene to 5:6-dihydroxyflavone (III)

Experimental

5-Benzeneazo-6-hydroxyflavone (IV).—A solution of diazobenzene chloride, prepared from aniline (2 g.; 2·5 mol.), concentrated hydrochloric acid (6 c.c.), alcohol (30 c.c.) and sodium nitrite (1·8 g. in 10 c.c. water), was gradually added at 0° to a solution of 6-hydroxyflavone (2 g.) in alcohol (50 c.c.), pyridine (14 c.c.) and ammonia (*d.* 0·88, 2 c.c.). During addition of the diazo solution and for six hours thereafter, the mixture was mechanically stirred and maintained at 0·5°. On leaving overnight, the dark red precipitate was collected, boiled with hot 50% hydrochloric acid for a few minutes, filtered, washed, and crystallised from alcohol. The dark red, elongated plates (2 g.) melted at 191–92° (Found: N, 8·4. $C_{21}H_{14}O_2N_2$ requires N, 8·2%).

5-Amino-6-hydroxyflavone (V).—5-Benzeneazo-6-hydroxyflavone (1 g.) was dissolved in boiling acetic acid (30 c.c.), and to the boiling solution zinc dust (2 g.) was added in small lots and the reaction mixture refluxed for 20 minutes. The deep red solution became brown in colour. Zinc dust (0·5 g.) was added, and the solution refluxed for 20 minutes longer. The solution was filtered and the zinc dust extracted thrice with 5 c.c. portions of hot acetic acid. The filtrate was cooled, diluted with water and allowed to stand in the refrigerator. The yellowish brown precipitate was filtered, washed with water, sucked dry, and dissolved in hot alcohol (Norit). The filtered alcoholic solution was diluted with water and allowed to stand in the refrigerator. The orange-brown clusters of needles were collected and dried *in vacuo*. The substance (0·5 g.) melted at 235° after shrinking at 200° (Found: N, 5·7. $C_{15}H_{11}O_2N$ requires N, 5·5%). The brown alcoholic solution turns dark greenish brown on the addition of ferric chloride. The substance dissolves in caustic soda giving an orange brown colour. It gives a pale brown colour with concentrated sulphuric acid. It gradually goes into a pale brown solution by boiling with N-hydrochloric acid.

Flavone-5-diazo-6-oxide (VI).—5-Amino-6-hydroxyflavone (0·5 g.) was boiled with N-hydrochloric acid (20 c.c.), till most of it went into solution. The solution was filtered, and the residue twice extracted with 20 c.c. portions of the acid. A small amount of undissolved resinous matter was rejected. The combined hydrochloric acid extracts were cooled to room temperature and sodium nitrite (2 g.) was added in small lots, the reaction flask being rotated during addition. On leaving the reaction mixture in the refrigerator for 30 minutes, the yellowish brown precipitate was filtered, washed with water and dried. There was no appreciable change in the yield by carrying out the sodium nitrite addition at 10° or 50°. Crystallised from alcohol,

glistening brown needles were obtained, which decomposed at 173°. (Found: C, 68 2; H, 3·1; N, 10 4. $C_{15}H_8O_3N_2$ requires C, 68·2; H, 3·0; N, 10·6%.) The substance does not respond to Lassaigne's sodium fusion test for nitrogen. It is insoluble in aqueous caustic soda, and dissolves in concentrated sulphuric acid with a yellow colour. The alcoholic solution gives no colouration with ferric chloride The method of preparation, the colour of the substance, its instability to heat and other properties are characteristic of the diazo oxides [4]

5:6-*Dihydroxyflavones* (III).—To a boiling mixture of concentrated sulphuric acid (10 c c) and water (10 c.c) the flavone diazo oxide (VI) (0 1 g) was added in small lots It immediately went into solution with frothing, a reddish brown solution being formed Boiling was continued for five more minutes, the solution allowed to cool, and diluted with water On letting stand in the refrigerator, the yellowish brown precipitate was filtered, washed free from acid, and twice crystallised from dilute alcohol. The honey-yellow needles (0 03 g) melted at 189-90° (Found: C, 70·9; H, 4·3 $C_{15}H_{10}O_4$ requires C, 70 8; H, 3 9%) The alcoholic solution of the substance gives an intense olive green colour with ferric chloride; an orange red precipitate with lead acetate in alcohol; and a red insoluble sodium salt when aqueous sodium hydroxide is added The yellow solution in concentrated sulphuric acid exhibits no fluorescence

5:6-*Diacetoxyflavone*.—5. 6-Dihydroxyflavone (0·05 g) was dissolved in acetic anhydride (2 c c) and fused sodium acetate (0·5 g) added. The mixture was refluxed for 2 hours, poured over crushed ice, the greyish brown solid collected, washed with water and crystallised from alcohol (Norit) The pale yellow prisms melted at 164-65° (Found· C, 67 8; H, 4·3. $C_{19}H_{14}O_6$ requires C, 67 4; H, 4 2%)

While the properties of our dihydroxyflavone agree with those recorded for 5:6-dihydroxyflavone, the following table gives a comparison of the properties of 5:6-dihydroxyflavone[6] and 6:7-dihydroxyflavone [5] The latter would have been obtained if the coupling of 6-hydroxyflavone with diazobenzene chloride had taken place in the 7- instead of the 5-position.

Properties	5 : 6–Dihydroxyflavone	6 7–Dihydroxyflavone
Crystalline form	Honey yellow needles	Pale cream coloured silky needles
M.P	189–90°	254°
Ferric chloride	Intense olive green	Intense green
Concentrated sulphuric acid	Yellow non fluorescent solution	Colourless non fluorescent solution
Aqueous sodium hydroxide	Red insoluble sodium salt	Bright yellow solution
Alcoholic lead acetate	Orange red precipitate	Greenish yellow precipitate
Diacetyl derivative	Prisms, m p 164–65°	Needles, m.p. 201°

SUMMARY

It has been shown that 6-hydroxyflavone couples with diazo salts in the 5-position 5-Benzeneazo-6-hydroxyflavone has been reduced to 5-amino-6-hydroxyflavone Treatment of the latter with nitrous acid gave flavone-5-diazo-6-oxide, hydrolysis of which with boiling dilute sulphuric acid led to 5. 6-dihydroxyflavone.

The utility of the general procedure for the synthesis of other polyhydroxyflavones and methoxyhydroxyflavones is being studied

We are indebted to the Sir Dorab Tata Trust for a Research Fellowship awarded to one of us

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THE GLYCERIDE COMPOSITION OF FATS AND OILS

Part II. The Fatty Acids and Glycerides of *Terminalia belerica* (Roxb.)

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Oils of *Terminalia* genus have been little investigated Of the three more important species *Terminalia catappa*[1, 2] (Indian almond), *Terminalia chebula*[3] and *Terminalia belerica*,[4] only the first has been examined by the ester fractionation method; the oil from *Terminalia chebula* has merely been separated into saturated and unsaturated acids while *Terminalia belerica* oil does not seem to have been investigated in detail at all No member of this genus has been investigated with regard to the glyceride structure till now

The first examination of oil of *Terminalia belerica* seems to have been made by Hefter[5] who, however, has reported only that the seed kernel yields 44% of a fatty oil which consists of solid and liquid glycerides Hooper[6] has recorded some constants of two specimens of the oil We have now examined two specimens of the oil for component acids, one by ester fractionation procedure and the other by the simple but equally accurate Bertram procedure The component acids consist of palmitic and stearic with a little arachidic in the saturated series and probably only oleic and linoleic acids in the unsaturated class All the three species of *Terminalia* are characterised by the presence of about 25% of linoleic acid (see below) *Terminalia catappa* and *Terminalia belerica* show a closer resemblance in

	Weight percentage on total acids					
	Saturated				Unsaturated	
	C·14	C 16	C·18	C 20	Oleic	Linoleic
catappa—1 ..	1 0	29 0	4·1	0 6	41 7	23·4
2 ..	..	24·0	9·7	0·4	27·3	28·6
T. chebula ..	..	17 8	.	..	58·8	23 4
belerica						
Ester method ..	..	22 4	15·7	0 8	28·1	33·0
Bertram method ..	..	20·5	20·8	..	26·7	32·0

the large amount of saturated acids which they contain, though those of the latter consist principally of palmitic acid while those of the latter consist of about an equal mixture of palmitic and stearic

We have completed the examination of one specimen of *T belerica* oil (I.V. 78 5; Saturated acids 41·3%) for the constituent glycerides according to the oxidative method evolved in our laboratory[6, 10] The absence of fully saturated glycerides in any quantity was proved by a preliminary oxidation which gave only 0 0018 gram of neutral material from 6 grams of the oil. The mean molecular weight of the saturated acids was found to be 270 0 and 270 2 in two separate determinations, their percentages being 39·49 and 39·5 on the weight of the oil. Since fully saturated components were absent, washing of the ethereal solution of the acidic oxidation products leaves behind monoazelao-disaturated glycerides and diazelao-monosaturated glycerides together with any unoxidised fat The results of two typical examinations are detailed in the experimental section.

As shown in the experimental part, the percentage composition by weight of the component acids of the above specimen of *Terminalia belerica* oil is palmitic 20 50, stearic 20·80, oleic 26·70 and linoleic 32·0; which, as expressed by molecules, is palmitic 22 2, stearic 20·2, oleic 26·1 and linoleic 31·5; thus making a total of 42 4 molecules of saturated acids and 57·6 molecules of unsaturated acids. Of this, 18 6 molecules of saturated acids are combined as GS_2U and none as GS_3, hence the remaining 23·8 molecules are combined as GSU_2, thus forming 71 4 molecules of di-oleo-monosaturated glycerides and the final composition of the oil is GS_2 traces, GS_2U 28%, GSU_2 71·4% and GU_3 0·6% The glyceride composition as calculated by some methods of partitioning of the fatty acids among themselves[9] are shown in the accompanying table·

	GS_3	GS_2U	GSU_2	GU_3
Determined	Trace	28 0	71 4	0 6
Even distribution	0	27 3	71·7	0
Oleic among others	12 4	45 0	.	42 6
Linoleic among others	8·2	58 8	.	38·0
Oleic among others, then excess of linoleic over oleo dilinolene among saturated	.	59·9	7 4	32 7

The most striking aspect about the glyceride constitution of oil of *Terminalia belerica* is its close approximation to the rule of even distribution which is not met with in many of the other seed fats which we have examined so far. It would, at this point, be of interest to compare the glyceride

composition of a Mowra oil, which we have recently investigated[8] and which had practically the same saturated-unsaturated acid ratio. The component acids are the same and there is not much difference in their proportions except in the relative proportions of oleic and linoleic acids. But the glyceride structure is entirely different in the two cases. This shows that probably the general mode of construction or assembling of the acids into triglycerides need not be the same even in any two vegetable seed fats (compare Hilditch[9])

Experimental

Weight of oil oxidised	5·3788 grams
Weight of azelao glyceride mixture after washing with bicarbonate	3·1475 ,,
Saponification value of the mixture	359 1
Weight of recovered total saturated fatty acids	2 1450 ,,
Iodine value of recovered saturated acids	0·90

The iodine value 0·9 of the acids recovered corresponds to the unoxidised portion of the oil After Bertram separation, the weight of acids is 2 145 grams, which works up to, on the weight of oil, 2 145 × 100/5·3788 or 39·87%. The percentage of unsaturated unoxidised acid will be 0·9 × 39·87/90 or 0·398 on the weight of oil (90 being the iodine value of oleic acid) Since, for purposes of computation, the percentage of unsaturated glycerides (unoxidised) will be approximately thrice the unsaturated acids, the percentage of unoxidised unsaturated glycerides is 0 398 × 3 or 1·2

A more detailed calculation is as follows :—

282 of oleic acid should give [282 + (2 × 270) + 38] of GS_2U by weight when S is 270 (mean molecular weight in the present instance[5]) or 860 Here the assumption is that of the two mixed unsaturated glycerides (GS_2U and GSU_2) the GS_2U has greater probability of escaping complete oxidation.

The weight per cent. of GS_2U will be 0·398 × 860/282 or 1·205 per cent 1·2 per cent of the oil is contained in 3 1475 grams of the azelao glyceride mixture obtained experimentally Hence the percentage content of unoxidised oil based on the azelao-glycerides mixture will be

$$1·2 \times 5\ 3788/3·1475 \text{ or } 2·05.$$

The saponification value of 2·05% will be 56 11 × 100 × 3/860 or 195·7. Hence the S V of the mono-, and diazelao-glyceride mixture can be calculated. The actual experimental saponification value of the mixture containing GS_3, GS_2U, GS_2A and GSA_2 is 359·1. In this case of course, GS_2 is nil and hence we have now to correct for the saponification value of GS_2U.

If X is the saponification value of the mixture, GS_2A and GSA_2, then $359{\cdot}1 \times 100 = 195\ 7 \times 2{\cdot}05 + (X \times 97{\cdot}95)$, where 97·95 is the sum total of the percentage of GS_2A and GSA_2. Hence X is 362·3.

Weight of mixture of azelao-glycerides is $3{\cdot}1475 \times 97\ 95/100$ The percentage weight of mono-azelao-glycerides is

$$\frac{3{\cdot}1475 \times 97{\cdot}95 \times (410{\cdot}2 - 362{\cdot}3)}{100 \times 5\ 3788\ (410\ 2 - 293)} \times 100 \text{ or } 23\ 42,$$

since saponification value of GS_2A is 293·0 and of GSA_2 is 410·2 (experimental determination gave 410·8) and percentage of GSU_2 by weight is $23{\cdot}4 \times 860{\cdot}2/766{\cdot}2$, 1·2 or 27·5

In a duplicate experiment 4·4739 grams of oil were oxidised and 2·6020 grams of azelao-glyceride mixture was obtained after washing with bicarbonate. The mixture of glycerides had a saponification value of 358 4 After Bertram separation, the saturated acids obtained weighed 1·7778 grams The recovered saturated acids had an iodine value of 0 6. Hence percentage of unoxidised fat as oleo disaturated glycerides is 0·8, and percentage of unoxidised fat in azelao-glyceride mixture is 1 4. The percentage weight of azelao-glycerides is $58{\cdot}16 \times 98{\cdot}6/100$ True saponification value of azelao-glycerides is 360·6 Hence percentage weight of monoazelao-glycerides is

$58{\cdot}16 \times 86{\cdot}6/100 \times 49{\cdot}6/117{\cdot}2$ or 24·27

Percentage of GS_2U by weight is $24\ 27 \times 860\ 2/766{\cdot}2$, 0 8 or 28 0

Percentage of GS_2U in oil by weight is 27·5, 28·0/2, or 27·75.

Percentage of GS_2U in oil by molecules is 28 0.

Analysis of the Oil by Ester Fractionation—1941 *Sample*—187 grams of the seed kernel was exhausted with benzene yielding 74 4 grams of the oil corresponding to an yield of 39 8% 218 grams of the oil was hydrolysed yielding 203 grams of mixed acids of mean molecular weight 277·8; iodine value 87·36; Titre 35, Refractive index (40) 1 4524

The mixed acids separated into solid and liquid acids by lead salt separation yielded, approximately, 75 2 grams of solid acids and 127 8 grams of liquid acids. They gave the following analytical constants:—

	Solid Acids	Liquid Acids
Refractive Index ..	1·4434 (60)	1·4588
Mean Molecular weight ..	272·6	281·2
Iodine Value ..	1·8	129·4

100 grams of the solid and liquid acids were separately esterified and fractionated The solid acids fraction consisted of C_{16}—19·93; C_{18}—15·76; C_{20}—0·79; oleic—0·20; linoleic—0·32. The liquid acids fraction consisted of C_{16}—2 45, oleic—27 90 and linoleic—32·64 Hence the components are C_{16}—22·38, C_{18}—15·76; C_{20}—0·79, oleic 28 10 and linoleic 32·96 per cent

Distillation of Solid and Liquid Acid Esters

No	Weight	Temperature	S Equivalent	Refractive Index	Iodine Value
			(*a*) Solid acids		
1	31 48	190–195	293·80	1 4390	0·35
2	29·15	190–195	294·50	1 4390	0·44
3	12·46	195–205	302 20	1·4410	3 85
4	6 27	Residue	318 50	1 4625	14 50
			(*b*) Liquid acids		
1	29 04	200–205	306 4	1 4505	119·7
2	32·23	205–210	309 2	1 4507	123·7
3	20·25	210–215	308 8	1 4510	125·2
4	11 34	Residue		1 4624	118 2

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RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part IV. Barytes

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1. Introduction

Although large transparent single crystals of barytes are easily available, comparatively little work has so far been done on its Raman spectrum. Nisi (1929) and Krishnamurti (1930) who were the early investigators on this subject recorded only a couple of Raman lines. Using the 2536·5 λ mercury radiation as exciter, Rasetti (1932) recorded a spectrum with a specimen of barytes which exhibited as many as eight low frequency lines and eight lines due to the SO_4 ion with frequency shifts 56 8, 62 2, 73·6, 88·3, 97 8, 127 3, 150 4, 189 8, 451·4, 462·2, 631 1, 647·5, 989·3, 1104·6, 1141·4 and 1167·2 cm^{-1} Using the same technique and giving longer exposures Roop Kishore (1942) repeated the experiment Owing to the smaller dispersion of the spectrograph used by him, the number of Raman lines identified was less than that reported earlier by Rasetti Roop Kishore, however, succeeded in recording an additional fainter line at 1088 $cm.^{-1}$ and a weak band extending from 1200 $cm.^{-1}$ to 1300 $cm.^{-1}$ He found that the orientation of the crystal with reference to the direction of illumination and observation had a marked influence on the relative intensities of the lines.

Using the 4046 and 4358 λ radiations of the mercury arc Balakrishnan (1941) investigated the effect of crystal orientation on the Raman lines due to the internal oscillations of the SO_4 ion in barytes The specimen employed by him was in the form of a parallelepiped with its faces parallel to the cleavage planes (001), (110) and (1$\bar{1}$0) He claimed to have observed 15 distinct Raman lines with frequency shifts 452, 458, 614, 620, 638, 650, 989, 1038, 1082, 1088, 1109, 1136, 1142, 1158 and 1170 cm^{-1}, some of which did not appear for certain orientations of the crystal According to him, none of the three settings of the crystal tried by him gave the complete spectrum. This result has neither been confirmed nor contradicted by Roop Kishore (1942). From an analysis of the polarisation data Balakrishnan concluded that the lines with frequency shifts 452, 458, 650, 989 and 1170 $cm.^{-1}$ belonged to the symmetric class.

It is clear that the results obtained by the earlier investigators on the Raman effect in barytes are neither complete nor in agreement. It is therefore thought desirable to study the problem afresh using the very powerful ultra-violet technique which has yielded much useful information in the case of diamond, calcite, quartz, etc. (Krishnan, 1945). The use of the 2536 5 Å resonance radiation as exciter would enable one not only to record the first order spectrum of barytes in all its detail but also to investigate the nature of its second order spectrum about which nothing is known at present The present investigation was undertaken with this object in view and also to confirm or disprove Balakrishnan's findings regarding the effect of crystal orientation on the frequency shifts of the Raman lines.

2 Details of the Experiment

From Sir C. V Raman's personal collection of minerals two transparent specimens of barytes were chosen for the present study The bigger crystal was in the form of a parallelepiped (10 × 8 × 5 cm), with its faces parallel to the natural cleavage planes (001), (110) and (1$\bar{1}$0) It was used as such The smaller specimen which had a natural *c* (001) face was cut and polished with its faces perpendicular to the axes of the optical ellipsoid This crystal measured nearly 1 × 1 × 2 5 cm

The optical arrangement employed for recording the Raman spectrum using the mercury resonance radiation as exciter has been described in Part I of this series (Krishnan, 1945) Using the E 3 quartz spectrograph a preliminary investigation was carried out in order to find any variations in the frequency shifts of the Raman lines for different settings of the crystal Using the cut crystal three different spectrograms of the Raman effect were taken with the crystal illuminated successively along the *a*, *b* and *c* axes, the transversely scattered light being taken along *b*, *c* and *a* axes respectively A comparative study of the three spectra recorded in juxta-position on the same negative showed that the frequency shifts of the Raman lines remain invariant, whereas the relative intensities of the lines depend on the orientation of the crystal. The experiment was repeated with the bigger crystal which had the natural cleavage faces and the same result was obtained Balakrishnan's claim that none of the orientations of the crystal of barytes gave a complete Raman spectrum is therefore not substantiated by the results obtained by the author.

In order to get accurate measurements of the frequency shifts of the principal Raman lines, a Hilger E 1 quartz spectrograph which has a dispersion of about 50 wavenumbers/mm. in the 2536 Å region was used.

Using a slit width of 0·03 mm. and the bigger crystal, exposures of the order of 4 days were given to photograph the Raman spectrum showing the first order lines with reasonable intensity The frequency shifts of the lines were evaluated by comparison with the superposed iron arc spectrum.

In order to record the second order spectrum the high speed low dispersion E 3 quartz spectrograph was employed With a slit width of 0·03 mm exposures of the order of two to three days were given to get an intense spectrogram The frequency shifts of the more intense and easily identifiable second order lines were evaluated from measurements made on the spectrogram Those of the feebler ones were estimated from the microphotometric record

3 Results

A typical photograph of the Raman spectrum taken with the E 1 spectrograph together with its microphotometric record is reproduced in Fig 1 in Plate I. The positions and the frequency shifts of the principal Raman lines are marked in Fig 1 *b* They are listed in Table I. The figures

TABLE I

Principal Raman lines of barytes

No	Group	Frequency shifts in cm^{-1} author's value	Notations	Rasetti's value
1	Lattice	58 5 (6)	L_1	56·8
2	,,	64·0 (8)	L_2	62 2
3	,,	73 6 (10)	L_3	73·6
4	,,	88·3 (6)	L_4	88 2
5	,,	96 5 (4)	L_5	97·8
6	,,	127 4 (3)	L_6	127 3
7	,,	148 6 (3)	L_7	150 3
8	,,	151 4 (4)	L_8	
9	,,	189 7 (4)	L_9	189 6
10	Sulphate	452·9 (14)	ν_1	451 4
11	,,	462 2 (15)	ν_2	462 2
12	,,	617·1 (10)	ν_3	..
13	,,	630·3 (7)	ν_4	631 1
14	,,	648 3 (8)	ν_5	647 5
15	,,	988·6 (30)	ν_6	980 3
16	,,	1084 2 (6)	ν_7	1104·6
17	,,	1104·2 (5)		
18	,,	1139 1 (10)	ν_8	1141 4
19	,,	1144 8 (10)		
20	,,	1167·2 (8)	ν_9	1167·2

given in brackets represent visual estimates of the relative intensities of the lines The direction of illuminaton was normal to the (001) face and the direction of observation was normal to the (110) face Rasetti's values for the frequency shifts are shown in column 5. The author's results are in

close agreement with those of Rasetti except for the three doublets with frequency shifts 148·8-151 4 cm.$^{-1}$, 1084 2-1104 2 cm^{-1} and 1139·1-1144 8 cm.$^{-1}$ Rasetti treated them as single lines. The principal Raman line

TABLE II

Second order Raman lines of barytes

No	Frequency shifts in cm^{-1}	Assignment	Calculated frequency shifts
1	170	$L_2 + L_5$	170
2	246	$L_5 + L_7$, $L_5 + L_8$	245, 248
3	273	$L_6 + L_7$	276
4	293	$2L_7$	298
5	341	$L_8 + L_9$	341
6	518	$\nu_1 + L_2$	517
7	542	$\nu_1 + L_4$	541
8	750-800	$\nu_3 + L_6$, $\nu_4 + L_6$	744 ; 767, 766
		$\nu_3 + L_7$; $\nu_5 + L_6$	775, 797, 799
		$\nu_5 + L_7$, $\nu_5 + L_8$	
9	900	$2\nu_1$	906
10	923	$2\nu_2$	924
11	967		
12	1216	$\nu_3 + L_8$	1215
13	1238	$2\nu_3$	1235
14	1267	$\nu_3 + \nu_5$	1266
15	1439	$\nu_4 + \nu_1$	1442
16	1450	$\nu_4 + \nu_2$	1451
17	1603	$\nu_4 + \nu_3$	1606
18	1970	$2\nu_4$	1978
19	2220	$\nu_1 + \nu_4$	2223

with the frequency shift of 617·1 cm^{-1} has been recorded for the first time. The 20 Raman frequencies tabulated above have been classified into two groups, namely, lattice spectrum denoted by L_1, L_2, ... L_9 and the spectrum of the SO_4 ions in the crystal denoted by ν_1, ν_2, ... ν_9

An intense photograph of the Raman spectrum of barytes taken with the E 3 spectrograph is reproduced in Fig 2 together with a spectrum of the mercury arc for purposes of comparison. The corresponding microphotometric records are shown in Fig 3 The second order Raman lines can be clearly seen on the microphotometric record Most of them can also be identified on the reproduced photograph. In addition to the 20 Raman lines belonging to the first order spectrum, there are not less than 18 Raman lines and one Raman band constituting the spectrum of the second order. The frequency shifts of these are listed in Table II. They have all been recorded as such for the first time Roop Kishore (1942) reported the existence of only a band extending from 1198 cm^{-1} to 1300 cm.$^{-1}$ consisting of unresolved lines.

Of the second order lines, the Raman line with the frequency shift 967 cm.$^{-1}$ is the most intense one as it appears even in the lightly exposed photograph taken with the E 1 spectrograph. See Fig. 1 The pair of lines with frequency shifts 1216 cm^{-1} and 1238 comes next in the order of intensity.

As in the case of other crystals like calcite, gypsum, etc., the intensity of the 2536·5 λ line relative to that of its companion at 2534 8 λ is greater in the spectrum of the scattered light than in that of the direct arc The enhanced intensity of the unmodified line can be attributed to the presence of Brillouin components which are not absorbed by the column of mercury vapour, compare the microphotometric records reproduced in Fig 3.

4 Discussion

Barytes is an ionic crystal belonging to the orthorhombic bipyramidal class. The unit cell contains four molecules of $BaSO_4$, the space group is V_h^{15} James and Wood (1925) carried out a detailed X-ray analysis of the crystal structure of barytes Their results go to show that the SO_4 ions preserve their tetrahedral symmetry in the crystal.

Spectrum of the SO_4 ion.—The SO_4 ion in the free state has only four distinct modes of oscillation with frequency shifts 454 (2), 622 (3), 983 (1) and 1106 (3) cm.$^{-1}$ The figures given in brackets are the respective degeneracies. From group theoretical analysis Bhagavantam (1938) showed that in the case of anhydrite which belongs to the orthorhombic class the four distinct modes of oscillation characteristic of the free SO_4 ions split up into nine components in the crystal We may expect to get similar results with barytes also which has a structure similar to that of anhydrite With the disappearance of the degeneracy, the spectrum of barytes should exhibit all the nine lines characteristic of the SO_4 ion Actually 11 frequency shifts are recorded in the first order spectrum all of which are attributable to the oscillations of the SO_4 ion By comparing the values of the frequency shifts of barytes with those of the free SO_4 ion it is possible to identify seven out of the expected nine modes These are denoted by ν_1, ν_2, ν_3, . . ν_6 and ν_9 (see Table I) The remaining two fundamentals, namely ν_7 and ν_8 appear to have suffered a Fermi splitting due to accidental degeneracy giving rise to 4 Raman lines as indicated below It is probably correct to take ν_7 as 1094 cm^{-1} which splits up into 1084 and 1104 cm.$^{-1}$ on account of the fact that the combination ν_2 (462 2) + ν_4 (630 3) falls on the top of ν_7 In same way, ν_8 which has a frequency shift of 1142 cm^{-1} splits up into two lines with frequency shifts 1139 and 1145 cm.$^{-1}$ since the combination of ν_6 (988·6) and L_6 (151·4), one of the lattice lines falls in the region of this doublet.

TABLE III

Raman frequencies of the SO_4 ion

In the free state	454 Double		622 Triple			983 Single	1106 Triple		
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
In barytes ..	452·9	462 2	617 1	630 3	648 3	988 6	1094	1142	1167
In anhydrite	415	499	609	628	674	1018	1108	1128	1160
In gypsum ..	415	492	618	622	672	1006	1115	1138	1144

The values of the frequency shifts of the nine Raman lines due to the internal oscillations of the SO_4 ions in barytes, anhydrite and gypsum are listed in Table III. The corresponding Raman frequencies of the free SO_4 ion are also included for comparison The values of the frequency shifts for anhydrite were those reported by other workers. The values for gypsum were taken from Part II of this series (Krishnan, 1945) A comparative study of the frequency shifts of the SO_4 ion in barytes and anhydrite shows that the influence of the cation on the splitting of the degenerate frequencies 454 cm.$^{-1}$ and 622 cm.$^{-1}$ and on the enhancement of the totally symmetric oscillation frequency 983 cm^{-1} of the free SO_4 ion is inversely proportional to its atomic weight. Polarisation studies made by Rousset and Lochet (1945) show that in the case of gypsum the frequencies ν_1, ν_2, ν_4, ν_6 and ν_9 come under the symmetric class, whereas in the case of barytes Balakrishnan's measurements indicate that ν_1, ν_2, ν_3, ν_6 and ν_9 come under the symmetric class The fact that out of the nine SO_4 lines of barytes, five come under symmetric class and four antisymmetric shows that the vibrating SO_4 ion possesses only as elements of symmetry a binary axis parallel to the binary axis of the crystal, although the ion has the full tetrahedral symmetry when the atoms are at rest.

The lattice spectrum —Bhagavantam (1938) has shown that in anhydrite which has a structure similar to that of barytes there should be eighteen Raman active lattice oscillations. The recorded spectrum of barytes, on the other hand, consists of 9 lattice lines, *i e*, exactly half the theoretical number. Comparing the lattice spectrum of gypsum with that of barytes one finds that there is no striking similarity between the two except for the fact that both the spectra consist of sharp, intense and closely spaced lattice lines.

Combinations of the principal frequencies.—In the second order spectrum the overtones and combinations of all the fundamental frequencies listed

in Table I can appear On this basis satisfactory assignments have been given to all the lines except one with frequency shift 967 cm.$^{-1}$ appearing in the second order Raman spectrum (see Table II). The calculated frequency shifts agree reasonably well with the observed values. Of the sulphate frequencies, the octaves of ν_1 (452·9), ν_2 (462 2), ν_3 (617·1) and ν_3 (988 6) are recorded as clearly resolved lines There is indication of some unresolved lines in the neighbourhood of 1238 and 1267 cm^{-1} (see Fig. 3). These can be assigned as the octaves of ν_4 (630·3) and ν_3 (648 3). It is interesting to note that the octave of the most intense principal Raman line, namely, ν_1 (988·6 cm^{-1}) is very weak compared to the octave of some of the other sulphate lines, *e.g.*, ν_1 (452·9 cm^{-1}) or ν_2 (462·2 cm.$^{-1}$).

5 Infra-Red Spectrum

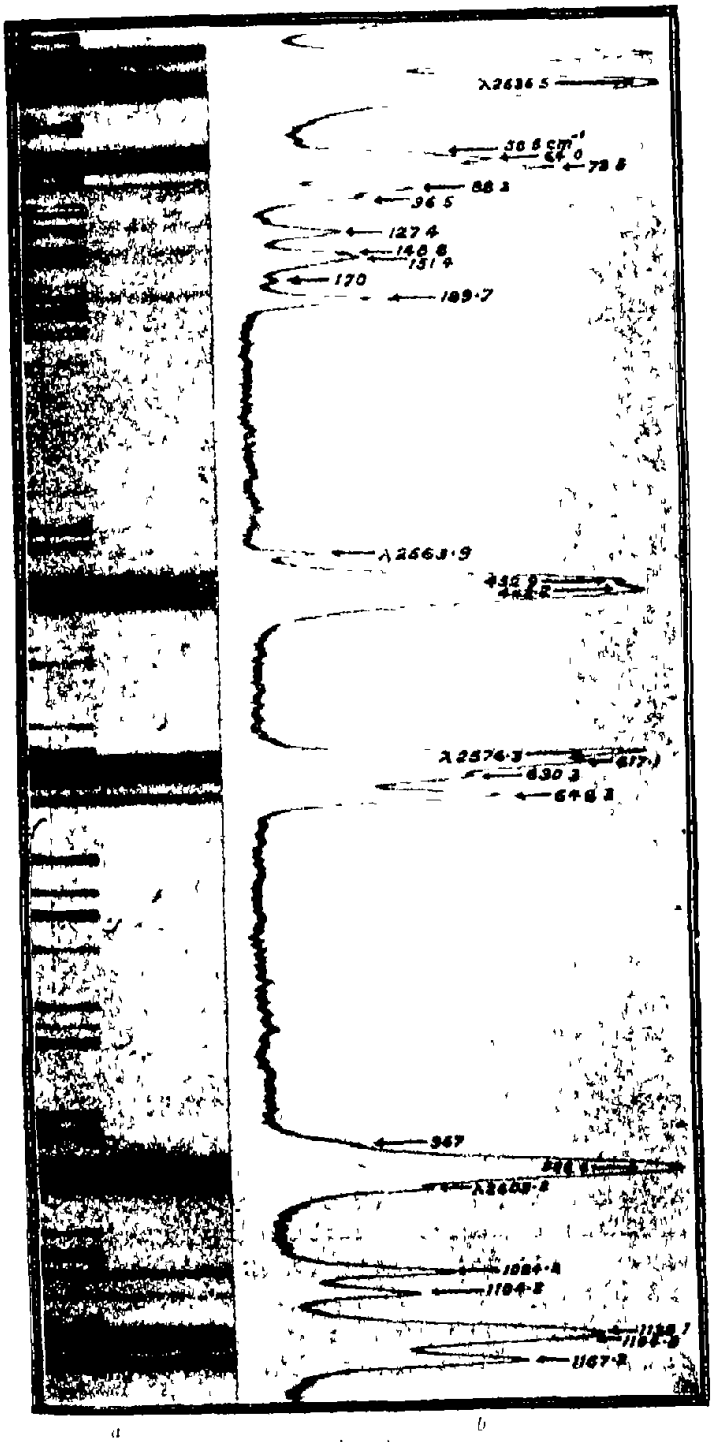
Comparatively little work has so far been done on the infra-red absorption spectrum of barytes. Schæfer and Schubert (1916) reported the existence of two reflection maxima in barytes, one at 8·30 μ (1204 cm^{-1}) and the other at 8 93 μ (1120 cm^{-1}) Matossi and Kindler (1934) investigated the infra-red absorption spectrum of barytes in the range from 2 μ to 16 μ. They observed two strong absorption bands at 9 μ and at 15 65 μ corresponding frequencies being 1100 cm^{-1} and 640 cm^{-1} These absorption bands might correspond to the observed Raman lines 630·3 and 1094 cm^{-1} which come under the antisymmetric class and hence active in the infra-red The above authors have also reported the existence of two weak absorption bands at 12 35 μ (810 cm^{-1}) and 10 81 μ (925 cm^{-1}) in the infra-red There are no first order Raman lines corresponding to these The second order spectrum, on the other hand, exhibits two Raman lines with corresponding frequency shifts.

The author is grateful to Sir C. V. Raman for the loan of the crystals of barytes and also for his interest in the work. The author is also indebted to the authorities of the Annamalai University for the loan of the Hilger E 3 quartz spectrograph

Summary

The previous work on the Raman effect in barytes has been briefly reviewed

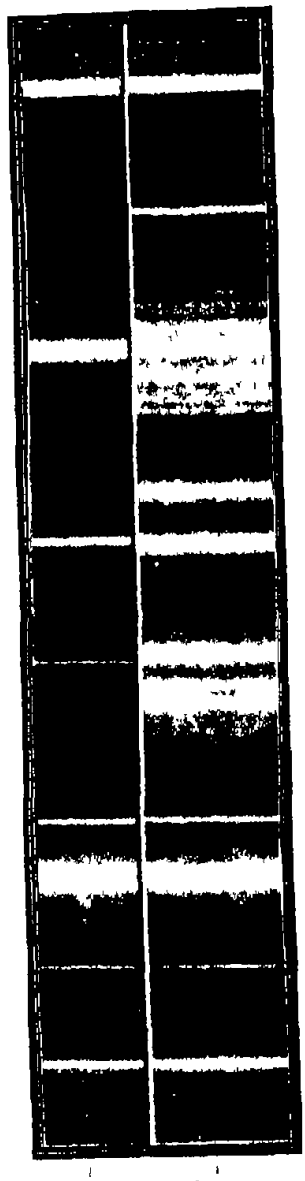
The Raman effect in natural crystals of barytes has been studied in detail using the 2536·5 Å mercury resonance radiation as exciter. The recorded spectrum consists of not less than 39 Raman lines nearly half of which have been recorded for the first time Of these 20 lines belong to the first order Raman spectrum and are distributed as follows.—9 lattice lines and 11 lines



a b

FIG. 1

(a) Raman spectrum of barytes taken with the E1 spectrograph
(b) its microphotometric record



1 2

FIG. 2

(1) Raman spectrum of barytes taken with the E3 spectrograph
(2) Comparison spectrum of the

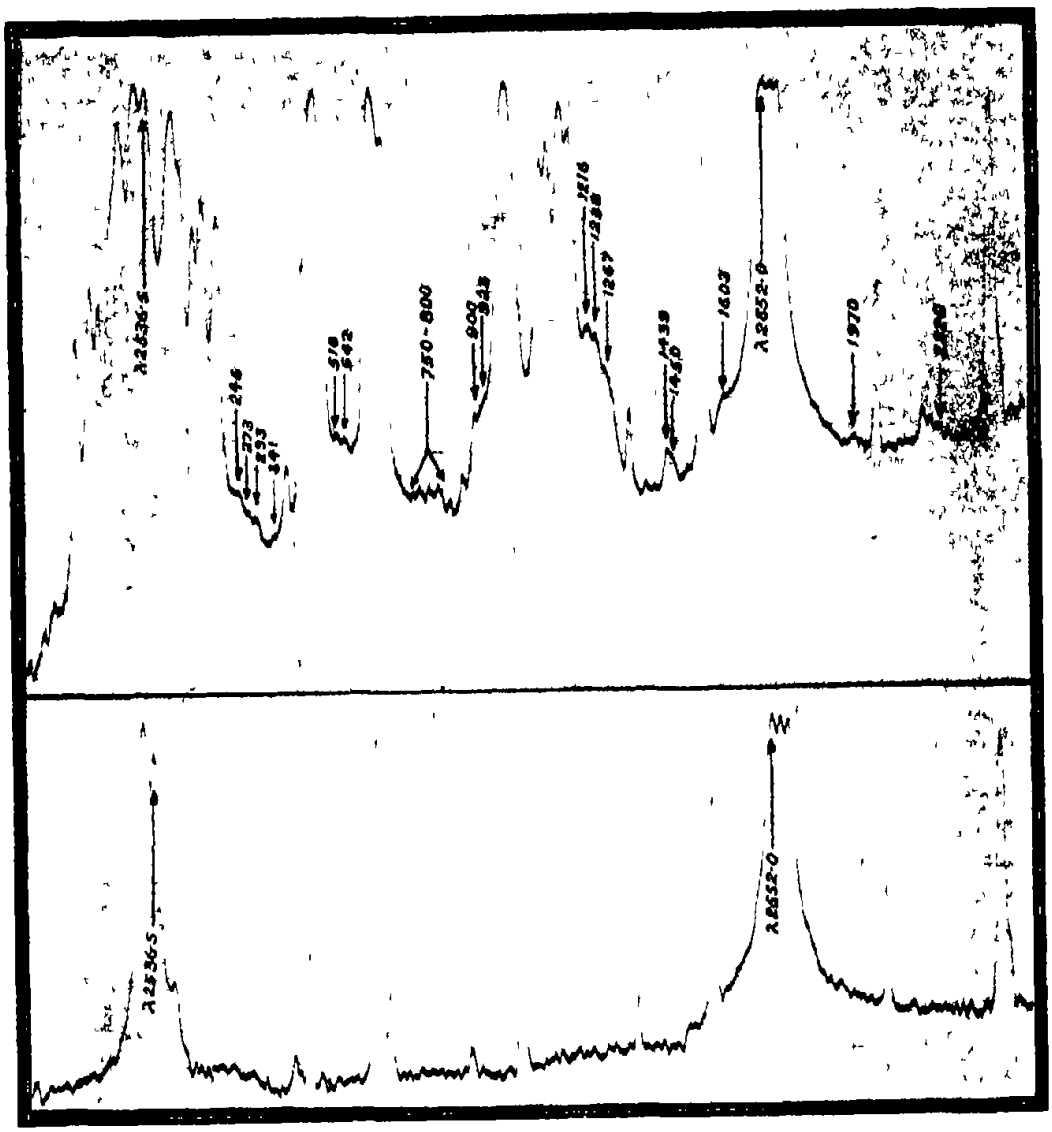


Fig. 3

(*a*) Microphotometric record of the Raman spectrum of butyles taken with the F3 spectrograph

(*b*) Microphotometric record of the mercury spectrum

due to the internal oscillations of the SO_4 ion. The frequency shifts of these lines have been accurately measured. The appearance of 11 Raman lines in the first order spectrum of the SO_4 ion has been satisfactorily explained on the basis of the lower order of symmetry of barytes crystal and also due to Fermi resonance splitting.

19 Raman lines of comparatively feeble intensity which constitute the second order spectrum have been assigned as octaves and combinations of some of the 20 principal Raman frequencies.

The frequencies corresponding to the maxima observed in the infra-red absorption spectrum of barytes have been compared with those observed in the Raman effect

A complete bibliography on the Raman effect and infra-red studies in barytes is included

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4. *General*

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CONSTITUTION OF CANNABISCITRIN—PART II

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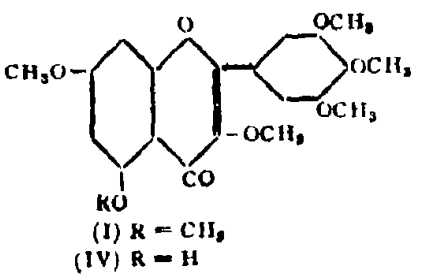
Received February 26, 1946

CANNABISCITRIN[1] is the main crystalline component of the flowers of *Hibiscus cannabinus* It is a monoglucoside of cannabiscetin, a flavonol having six hydroxyl groups When decomposed with aqueous alkali its hexamethyl ether yielded *O*-trimethyl-gallic acid Thus four of the six hydroxyl groups of the flavonol could be definitely allotted to the positions 3, 3′, 4′ and 5′ The orientation of the other two as 5·8 was tentatively suggested, based on colour reactions. The aglucone was considered to be isomeric with myricetin and not identical with it mainly for the following reasons. (1) it gave the gossypetone reaction though not so readily as gossypetin and this was considered to be characteristic of compounds having hydroxyl groups in the *para*-positions 5 and 8, it further gave a display of colours in alkaline buffer solutions, (2) the methyl ether of cannabiscetin as originally obtained was noticed to have a higher melting point than that of myricetin though the melting points of cannabiscetin and its acetate agreed with those of myricetin and its acetate

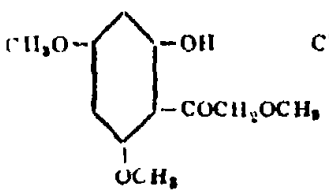
In a subsequent paper[2] the position of the sugar group was fixed as 3′. This was done by methylation of the glucoside, hydrolysis and fission of the product whereby 3-hydroxy-4. 5-dimethoxy-benzoic acid was obtained and identified

Further work has now been done with a view to obtain more definite information about the nature of the flavonol and its glucoside using improved methods of methylation and fission leading particularly to the isolation and identification of the ketonic decomposition product. The different methods of methylation that have been so far employed by different workers have been applied to the present case. The use of dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone solution has been found to be the most satisfactory and has given the best yields of the pure ether. The hexamethyl ether of cannabiscetin obtained in this way is found to melt at 156° agreeing with the melting point of myricetin methyl ether.[3] The higher melting product originally described could not be obtained again even by adopting the other methods and the older sample was not available for comparison due to loss during the transfer of our laboratories as a war measure. Whether this is antoher case of dimorphism found in certain other flavonol ethers could not therefore be settled.

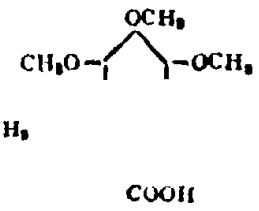
Since it has been our experience that the use of absolute alcoholic potash for the fission of methyl ethers gives much better results than older methods and is particularly suited for dealing with small quantities, this method has now been adopted for the fission of the hexamethyl ether of cannabiscetin (I). Besides trimethyl gallic acid (III) good yields of a ketonic product has been obtained and it has been identified as methoxy fisetol-dimethyl ether (II)[4] by a detailed study of its reactions and conversion into derivatives and also by comparison with a synthetic sample This definitely established the position of the two hydroxyl groups in the benzopyrone part as 5. 7 and not 5 8 and thus cannabiscetin should be the same as myricetin (VIII) The identity was established by the synthesis of myricetin and its derivatives according to the method of Kalff and Robinson[5] and comparison with cannabiscetin, its acetate and methyl ether It should be noted here that the colour reactions with buffer solutions and *p*-benzoquinone which were originally considered to be characteristic of the 5 : 8 arrangement of hydroxyl groups are also given by flavonols containing three hydroxyls in the 3′ 4′ · 5′ positions



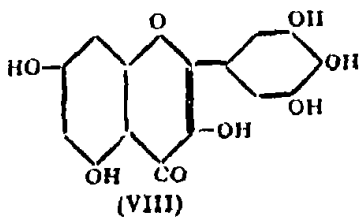
(I) R = CH_3
(IV) R = H



(II)



(III)



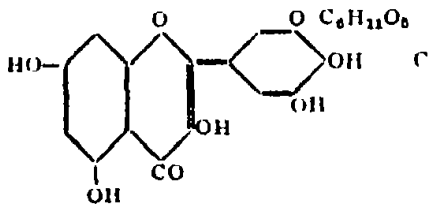
(VIII)

In the course of the experiments on the identification of cannabiscetin, methoxy-fisetol-dimethyl ether (ω. 4 : 6-trimethoxy-2-hydroxy acetophenone) was fused with the anhydride and sodium salt of trimethyl-gallic acid. There was partial demethylation during the condensation and the product was found to be 5-hydroxy-3. 7 3′. 4′ 5′-pentamethoxyflavone (IV) or pentamethylmyricetin[6] obtained by Perkin by the partial methylation of myricetin.

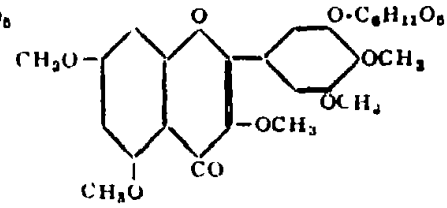
In the light of the identity of cannabiscetin with myricetin, the constitution of the glucoside, cannabiscitrin has been further investigated using the simpler

method of methylation. Though the glucoside is sparingly soluble in dry acetone, it could be successfully and fully methylated in this medium in a finely powdered condition by boiling with excess of dimethyl sulphate and potassium carbonate. The methylated glucoside could be obtained in a pure condition and hydrolysed to give a pentamethyl ether of cannabiscetin (myricetin) in good yield Fission of this substance with alcoholic potash has yielded as one product methoxy-fisetol-dimethyl ether (II) showing conclusively that the sugar group is not present in the benzopyrone part. The acid decomposition product was identified to be 4. 5-dimethyl gallic acid (IX) by comparison with a sample synthesised according to the method of Shriner and McCutchen[6] thus establishing the constitution of the pentamethyl ether as (VII) and the constitution of the glucoside as (V) with the sugar unit in the side phenyl nucleus in position 3'

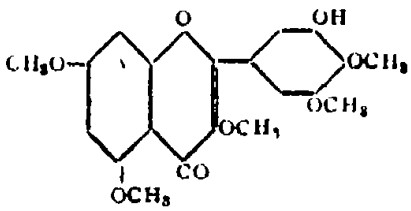
A more convenient method of establishing the exact constitution of the glucoside is to ethylate the above penta-methyl ether to give ethyl-pentamethyl-cannabiscetin (myricetin) (X) and subject this to fission. The reaction goes more smoothly yielding the same ketone (II) and 3-ethyl-4. 5-dimethyl gallic acid (XI) which is identical with the ethylation product of 4 5-dimethyl gallic acid These reactions are represented below·



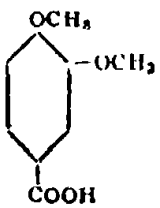
(V)



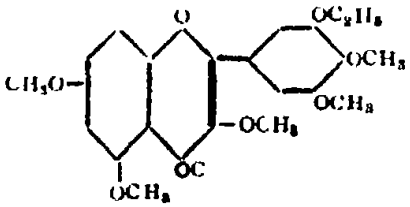
(VI)



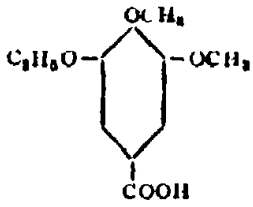
(VII)



(IX)



(X)



(XI)

Cannabiscitrin is, therefore, a new mono-glucoside of myricetin, the glucose group being in the 3'-position. Myricitrin[8] isolated by Perkin from *Myrica nagi* is a rhamnoside and the rhamnose unit is considered to be linked to the 3-position of the flavonol

It is interesting to compare the flavonols present in the flower petals of the two closely related species of *Hibiscus*, *H cannabinus* and *H sabdariffa*. Botanically the plants resemble closely and they are also used for the same purposes, as acid vegetables and as sources of fibre The *cannabinus* flowers contain myricetin as the flavonol, whereas hibiscetin is the main component of *sabdariffa* petals Since the latter is 8-hydroxymyricetin, it appears that the species difference rests in the oxidation of the 8-position of the flavonol molecule

Experimental

Hexamethyl cannabiscetin (I)—Cannabiscetin (1·0 g), dissolved in dry acetone (100 c c), was treated with dimethyl sulphate (2·5 c.c) and anhydrous potassium carbonate (20 g) and the mixture boiled under reflux for 30 hours After the completion of the reaction, the potassium salts were filtered off and washed with more acetone The filtrate was concentrated and the residue treated with water (100 c c); the methyl ether then separated out completely during the course of one hour. It was twice crystallised from dilute alcohol when it came out in the form of colourless rectangular plates and prisms melting at 155-56° It was insoluble in dilute sodium hydroxide solution and did not give any colour with alcoholic ferric chloride The methyl ether exhibited a weak blue fluorescence in alcoholic solution Yield· 1·0 g (Found C, 62·9, H, 5·7, OCH_3, 46·1, $C_{21}H_{22}O_8$ requires C, 62·7, H, 5·5; OCH_3, 46·3%) The mixed melting point with myricetin hexamethyl ether was undepressed

The use of benzene as the solvent in the above experiment also yielded the same methyl ether; the only difficulty was that cannabiscetin was not easily soluble in this solvent Still the yield and the quality of the product were unaffected

Other methods using (1) methyl iodide and anhydrous potassium carbonate in acetone solution, (2) methyl iodide and alcoholic potash and (3) dimethyl sulphate and alkali on cannabiscetin acetate, were examined in order to see if any higher melting ether could be obtained. But all of them yielded the same substance melting at 155–56°.

Decomposition of hexamethyl cannabiscetin with alcoholic potash : Isolation of trimethyl gallic acid (III) *and the ketone* (II).—Hexamethyl canna-

biscetin (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c. of 8%) for six hours under anhydrous conditions. At the end of the period as much of the alcohol as possible was distilled off and the residue dissolved in water. The aqueous solution was then filtered from a little insoluble impurity and the clear filtrate acidified with dilute sulphuric acid with cooling. The precipitated solid was then thrice extracted with ether and the combined ether solution shaken with 5% sodium bicarbonate to remove the acid part (A) On evaporating the ether solution the required ketone was obtained It was crystallised twice from dilute alcohol when it came out in the form of thin colourless plates melting at 104–05° The yield of the pure ketone was 0 34 to 0 38 g It could also be crystallised from hot water It dissolved easily in aqueous sodium hydroxide forming a pale yellow solution and gave a greenish brown colour with alcoholic ferric chloride The mixed melting point with an authentic sample of 2-hydroxy-ω-4 : 6-trimethoxy-acetophenone was undepressed (Found: C, 58 6, H, 6 5, OCH_3, 40 9; $C_{11}H_{14}O_5$ requires C, 58 4, H, 6 2, and OCH_3, 41·2%)

The *dinitrophenylhydrazone* was obtained by heating a mixture of the above ketone (0·1 g) and 2. 4-dinitrophenylhydrazine (0 2 g.) dissolved in alcohol (10 c c), on a water-bath for half an hour The phenylhydrazone separated out on cooling, it was washed with dilute hydrochloric acid and crystallised from alcohol when it came out in the form of orange-red micro-crystals melting at 160–62° It was soluble in aqueous alkali to give an orange-red solution (Found· C, 49 9, H, 4 7; $C_{17}H_{16}O_8N_4$ requires C, 50 2; H, 4 4%)

The clear bicarbonate solution (A) obtained above was neutralised with dilute hydrochloric acid The precipitated solid was repeatedly crystallised from hot water using a little animal charcoal. It came out in the form of colourless rectangular plates, melting at 167–68° and was identified as trimethyl gallic acid. The mixed melting point with an authentic sample of trimethyl gallic acid was undepressed. (Found: C, 56·7; H, 5 7, OCH_3, 44·1; $C_{10}H_{12}O_5$ requires C, 56 6; H, 5 7 and OCH_3, 43 9%)

ω·2 4 6- *Tetramethoxy-acetophenone* — 2-Hydroxy-ω-4 : 6-trimethoxy-acetophenone (0·2 g) was methylated in acetone solution with dimethyl sulphate (0·5 c c) and anhydrous potassium carbonate (5·0 g). The product was crystallised from dilute alcohol when it came out in the form of colourless rectangular plates melting at 151–52° It was insoluble in dilute sodium hydroxide solution and did not give any colour with alcoholic ferric chloride. (Found. C, 60·1; H, 6·9; OCH_3, 51 9; $C_{12}H_{16}O_5$ requires C, 60·0; H, 6 7 and OCH_3, 51 7%)

Comparison of cannabiscetin and myricetin (synthetic)—The following properties were compared and found to be identical The flavonols decomposed above 350° and gave a dark brown colour with alcoholic ferric chloride; the hexamethyl ethers melted at 155–56° and the hexa-acetates at 220–21°. The colour reactions in alkaline buffer solutions were also identical With freshly made buffer solutions, the appearance of pure blue has now been noticed even with a slightly lower pH. This may be due to changes in the buffer solutions during storage.

Condensation of hydroxy-fisetol trimethyl ether (II) *with the anhydride and the sodium salt of trimethyl gallic acid Preparation of 5-Hydroxy-3 7.3' 4'. 5'-pentamethoxy-flavone (IV)*—2-Hydroxy-ω.4 6-trimethoxy acetophenone (1·0 g.) was intimately mixed with the dry anhydride (6 g.) and the sodium salt of trimethyl gallic acid. The product was heated at 180° for 6 hours *in vacuo* The hard mass was then broken up and dissolved in alcohol (150 c c) and while boiling, an aqueous potassium hydroxide solution (8 g in 15 c c.) was added during the course of 20 minutes to decompose the excess of the anhydride The alcohol was then completely removed under reduced pressure and the residue dissolved in water. A small quantity of a solid (S) separated out. It was filtered and the filtrate was then saturated with carbon dioxide The pale yellow product was repeatedly crystallised from alcohol when it came out as very pale yellow stout needles melting at 140–41° This product corresponded to the pentamethyl ether of myricetin (m.p 138–39°) recorded by Perkin.[3] In bulk, the substance appeared yellow It gave an olive green colour changing to brown with alcoholic ferric chloride and did not exhibit any visible fluorescence in alcoholic solution (Found· C, 62 0, H, 5 3, OCH_3, 40 1, $C_{20}H_{20}O_8$ requires C, 61 9; H, 5 2 and OCH_3, 40 0%) On working up solid (S) some more of the above 5-hydroxy compound was obtained

Methylation of the above 5-hydroxy-flavone with excess of dimethyl sulphate and anhydrous potassium carbonate in acetone solution yielded the hexamethyl ether of myricetin which crystallised from dilute alcohol as colourless rectangular plates and prisms and melted at 155–56°.

Acetate of cannabiscitrin—This was conveniently prepared by boiling the glucoside with acetic anhydride and a drop of pyridine, and crystallising the colourless product by dissolving in cold acetone and adding enough ethyl alcohol to start crystallisation. When prepared in this manner, it appeared as colourless needles and melted to a transparent liquid at 194° (Found; C, 54·4; H, 4 4; $C_{30}H_{30}O_{22}$ requires C, 54·5, H, 4 4%)

Methylation of cannabiscitrin : Preparation of the methylated glucoside (VI).—Finely powdered cannabiscitrin (4·0 g.) was suspended in dry acetone (200 c c.), treated with dimethyl sulphate (6·0 g.) and anhydrous potassium carbonate (25 g.) and the mixture boiled under reflux for 30 hours It was occasionally shaken to bring any unreacted cannabiscitrin into solution. The acetone solution was filtered, washed with more acetone and then concentrated when colourless crystals of the methylated glucoside separated out. It was recrystallised from methyl alcohol when it came out as shining needles and rectangular plates melting at 149–50° It was insoluble in dilute alkali and did not give any colour with alcoholic ferric chloride (Found· C, 56 4; H, 5 3, $C_{28}H_{30}O_{18}$ requires *C*, 56 7, H, 5 5%)

Hydrolysis of the methylated glucoside : Isolation of pentamethyl cannabiscetin (*myricetin*) (VII) —The whole of the product obtained above (VI) was boiled under reflux with 7% sulphuric acid (200 c c) for 2 hours The hot solution was filtered through a plug of cotton-wool to remove a small quantity of insoluble impurity that had separated out The pentamethyl ether crystallised out almost completely on cooling. It was recrystallised twice from alcohol when it came out in clusters of colourless needles The correct melting point of this compound is 220–22° It did not give any colour with alcoholic ferric chloride, but dissolved easily in dilute sodium hydroxide forming a pale yellow solution with no fluorescence Yield, 1·76 g. from 4 g of cannabiscitrin It developed a pale pink fluorescence in neutral alcoholic solution after some time (Found C, 61 5, H, 4 8, OCH_3, 40·2, $C_{20}H_{20}O_8$ requires C, 61 9, H, 5 2 and OCH_3, 40 0%)

The above pentamethyl cannabiscetin (0 5 g) was dissolved in acetone (20 c c) and methylated by boiling for 10 hours with excess of dimethyl sulphate and anhydrous potassium carbonate. The product was crystallised from dilute alcohol when it came out as colourless rectangular plates melting at 154–56° and was found to be identical with the hexamethyl cannabiscetin obtained by direct methylation

Decomposition of the above pentamethyl ether (VII) *with alcoholic potash : Isolation of* 4, 5-*dimethyl gallic acid* (IX) *and the ketone* (II) —Pentamethyl cannabiscetin (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c. of 8%) for a period of six hours. The product was worked up as before into the sodium bicarbonate soluble part (acid part) and the ketonic part. On crystallisation from alcohol, the ketone came out as colourless rectangular plates, melting at 104–05° Mixed melting point with 2-hydroxy-ω ; 4 ; 6-trimethoxy acetophenone was undepressed.

The bicarbonate solution was acidified and repeatedly extracted with ether; the residue obtained on evaporating the ether solution was twice crystallised from hot water using a little animal charcoal when it came out as rectangular plates and prisms melting at 192–94° It was found to be identical with 4:5-dimethyl gallic acid, the mixed melting point with an authentic sample of 4:5-dimethyl gallic acid being undepressed. (Found: C, 54 7; H, 5 4; OCH_3, 31·2, $C_9H_{10}O_5$ requires C, 54 5, H, 5 1 and OCH_3, 31·3%)

3'-Ethyl-3.5 7.4' 5'-pentamethyl cannabiscetin (myricetin) (X)—The above pentamethyl cannabiscetin was ethylated with ethyl iodide and anhydrous potassium carbonate in acetone solution The product was worked up as before and the ethyl ether was twice crystallised from dilute alcohol when it came out as stout rods and rectangular plates, melting at 155–56°. A mixed melting point with hexamethyl myricetin was considerably depressed. The product was insoluble in aqueous alkali and did not give any colour with alcoholic ferric chloride

Decomposition of ethyl-pentamethyl cannabiscetin (X) *with alcoholic potash Isolation of the ketone* (II) *and 3-ethyl-4.5-dimethyl gallic acid* (XI)—The ethyl pentamethyl ether (1·0 g) was subjected to fission with alcoholic potash following the procedure already described The ketonic part was found to be identical with 2-hydroxy-ω:4.6-trimethoxy-acetophenone The acid was crystallised from hot water using a little animal charcoal when it came out as colourless rectangular plates and prisms melting at 164° It was identified as 3-ethoxy-4 5-dimethoxy-benzoic acid The mixed melting point with an authentic sample of 3-ethoxy-4·5-dimethoxy-benzoic acid, prepared as given below was undepressed (Found C, 58 6, H, 6·4; $C_{11}H_{14}O_5$ requires C, 58·4; H, 6 2%)

4.5-Dimethyl gallic acid[6] (1 0 g) was ethylated using ethyl iodide (2 c c.), anhydrous potassium carbonate and anhydrous acetone The ether ester was obtained as a viscous liquid and it was hydrolysed by boiling with sodium hydroxide solution (20 c c of 20%) for one hour The clear solution was then acidified and the solid product crystallised from hot water when it came out as colourless rectangular plates and prisms melting at 164° (Found: C, 58 5, H 6 4, $C_{11}H_{14}O_5$ requires C, 58 4 H 6 2%)

SUMMARY

The methylation of the glucoside, cannabiscitrin and of the aglucone, cannabiscetin has now been effected by a more efficient method and the fission products examined. As the result cannabiscetin has been identified

as myricetin and the identity has been confirmed by comparison of the flavonol and its derivatives with synthetic samples It is noted that the reactions of flavonols having the pyrogallol side-phenyl nucleus exhibit many similarities with those given by flavonols having the 5:7.8-arrangement of hydroxyl groups. The condensation of hydroxy-fisetol-trimethyl ether with the anhydride and sodium salt of gallic acid yields pentamethyl-myricetin instead of the expected hexamethyl ether, partial demethylation having taken place in the 5 position during the course of the condendation

Methylation of the glucoside, cannabiscitrin yields a pentamethyl ether which forms on hydrolysis pentamethyl cannabiscetin (myricetin). Alkali fission of this compound gives the same ketone as the hexamethyl ether. The acid part is identified as 4:5-dimethyl gallic acid, thus locating the position of the sugar group definitely in the 3′ position of the flavonol. This result has been confirmed by ethylating the pentamethyl cannabiscetin and subjecting the ethyl ether to fission with alkali Besides the ketone already mentioned, the acid decomposition product is found to be 3-ethyl-4:5-dimethyl gallic acid by comparison with a synthetic sample. The synthesis of the ethyl-dimethyl gallic acid is described.

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4. ——— — *Ibid.*, 1911, 99, 1721
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6. Shriner and McCutchen — *J A C S*, 1929, 51, 2193

STUDIES IN THE FRIEDEL-CRAFTS REACTION

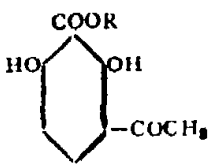
Part VIII. The Action of Acetic Anhydride on Methyl-γ-Resorcylate

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IN continuation of the previous work of Desai and Radha,[1] the action of acetic anhydride on methyl-γ-resorcylate in presence of anhydrous aluminium chloride has been studied. This condensation afforded methyl-2 · 6-dihydroxy-3-acetyl-benzoate (I, R = CH_3) and 2 . 6-dihydroxy-3-acetyl-benzoic acid (I, R = H) The ester and the acid both were characterized by the formation of 2 . 4-dinitrophenyl-hydrazones and semicarbazones The ester (I, R = CH_3) on hydrolysis afforded the corresponding acid (I, R = H), which on decarboxylation gave resacetophenone, thus establishing the structures of both the acid and the ester From the yield of the ester and the acid and the rate at which the reaction proceeded it was noted as expected that methyl-γ-resorcylate was more reactive than its isomer methyl-β-resorcylate.



(I)

EXPERIMENTAL

Methyl-2 . 6-dihydroxy-3-acetyl-benzoate (I, R = CH_3) and 2 6-dihydroxy-3-acetyl-benzoic acid (I, R = H). Finely powdered anhydrous aluminium chloride (3 g.) was dissolved in dry methyl-γ-resorcylate (2 g.) in nitrobenzene with constant shaking. Acetic anhydride (2·5 c.c) was then added to the mixture slowly and the mixture kept at room temperature for 24 hours, with an air condenser and a calcium chloride guard-tube attached to the flask. It was then heated for 3 hours on a water-bath and the mixture cooled. The aluminium chloride was decomposed by adding pieces of ice and hydrochloric acid to the reaction mixture and the nitrobenzene steam distilled The sticky paste obtained on cooling was worked up in the usual manner with sodium bicarbonate solution (5 per cent.) when part of it went into solution with effervescence, and a fraction remained insoluble. The

latter was washed with water and crystallized from very dilute hot alcohol in long golden-yellow needle., m p 137-38° C (Found. C, 56·9, H 4 4; $C_{10}H_{10}O_5$ requires C, 57 1; H, 4 8 per cent) It gave an intense red colouration with alcoholic ferric chloride and \ as very soluble in all the common solvents like alcohol, acetone and methyl alcohol

The sodium bicarbonate soluble portion was acidified with hydrochloric acid, and extracted with ether, when pale yellow micro-crystals were obtained on the evaporation of the solvents, m p 210-12° (Found: C, 54·8; H, 4 0; $C_9H_8O_5$ requires C, 55 1, H, 4 1 per cent) It gave effervescence with sodium bicarbonate solution and a wine-red colouration with alcoholic ferric chloride

The 2·4-dinitrophenyl-hydrazone prepared in the usual manner crystallized in orange-red micro-crystals from glacial acetic acid m p 293° (decomp) (Found: N. 14 2, $C_{16}H_{14}O_8N_4$ requires N, 14·4 per cent)

The Semicarbazone prepared as usual, crystallized in very pale-yellow, shiny micro-crystals from boiling alcohol, m p 273° (decomp) (Found: N, 15 4. $C_{11}H_{13}O_5N_3$ requires N, 15 7 per cent.)

2:6-dihydroxy-3-acetyl-benzoic acid (*I*, *R* = *H*) – Methyl 2: 6-dihydroxy-3-acetyl-benzoate (0 3 g) was hydrolysed in alcoholic alkaline solution in the usual manner The solid obtained on acidifying with hydrochloric acid, was purified through sodium bicarbonate solution (5%) The yellow solid obtained on acidification with hydrochloric acid was washed and crystallized from dilute hot alcohol in pale yellow micro-crystals, m p 209–10°. Mixed melting point with the previously obtained acid was unaltered.

Decarboxylation of 2: 6-dihydroxy-3-acetyl-benzoic acid (0·2 g.) by heating in a sealed tube with acidulated water (10 c c) at 160–70° for 5 to 6 hours yielded a sticky paste This was triturated with sodium bicarbonate solution and the insoluble portion crystallized from alcohol in yellow needles, m p. 145–46° Mixed melting point with an authentic specimen of resacetophenone was undepressed.

Summary

The action of acetic anhydride on methyl-γ-resorcylate in presence of anhydrous aluminium chloride afforded methyl-2 6-dihydroxy-3-acetyl-benzoate and 2: 6-dihydroxy-3-acetyl-benzoic acid.

Reference

1. Desai and Radha . *Proc. Ind. Acad Sci.*, 1940, 12 A, 46

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THE KINETICS OF THE OLEFINE-BROMINE REACTION

Part IV. The Rate Equation of the Homogeneous Catalysed Thermal Reaction

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Received March 7, 1946

A TENTATIVE mechanism for this reaction was proposed by the author[1] and this was subsequently modified[2] so as to bring the thermal mechanism in line with the photochemical change Since then, further work has shown that an examination of the results with a suitable reaction rate equation based on the mechanism is necessary and this constitutes the subject of the present communication

A homogeneous catalysed reaction such as the ones under consideration can involve activation of one or both of the reactants by the catalyst. Any derivation of the kinetic equation has to consider both alternatives The process of activation may involve the communication of the activation energy effectively to the molecules that would otherwise acquire it only very slowly and the molecules thus activated may react only after some interval during which they are liable to deactivation As postulated in the tentative mechanism, the catalyst may remain associated with the reactant as a complex which undergoes the reaction. The various processes taking place and the concentrations involved are collected in Table I

TABLE I

Process	Concentration	Rate Constant
Activation of reactant 1 ..	a_1	k_1
Deactivation of activated reactant 1	a_1	
Activation of reactant 2 ..	a_2	
Deactivation of activated reactant 2 ..	a_2	
Reaction between the activated reactants .	a_1, a_2	

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If the concentration of the catalyst is c, we get for the stationary concentration of the activated molecules the relation:

$$k_1 n_1 c - k_5 a_1 a_2 - k_2 a_1 c = 0$$
$$k_3 n_2 c - k_5 a_1 a_2 - k_4 a_2 c = 0.$$

From these two simultaneous equations, one gets

$$a_1^2 + a_1 (k_1/k_2\ n_1 - k_4/k_5 - (k_1/k_5\ k_4/k_5\ n_1 c) - (k_3/k_2 n_2) = 0$$

Neglecting the last term which involves neither the catalyst nor the reactant I and taking only the positive root of the quadratic for a_1, the reaction velocity equation

$$dx/dt = k_5 a_1 a_2$$

becomes

$$dx/dt = k_1 k_3 k_5\ n_1 n_2 c/k_2 k_4 c + k_1 k_5 n_1.$$

Applying this to the Olefine-Bromine reaction catalysed by hydrogen bromide we have

$$dx/dt = k_1 k_3 k_5\ [\text{Olefine}]\ [\text{Bromine}]\ \frac{[\text{Hydrogen Bromide}]}{k_2 k_4\ [\text{HBr}] + k_1 k_5\ [\text{Br}_2]} \qquad (1)$$

If one considers, however, that only one reactant gets activated by the catalyst, we get for the stationary state

$$k_1 n_1 c - k_5 a_1 c - k_5 a_1 n_2 = 0$$

and

$$dx/dt = k_5 a_1 n_2 + k_5 k_1 n_1 n_2 c/k_2 c + k_5 n_2.$$

This gives for the present reaction

$$dx/dt = k_5 k_1\ [\text{Olefine}]\ [\text{Bromine}]\ [\text{Hydrogen Bromide}]/k_2\ [\text{HBr}]\ k_5\ [\text{Olefine}] \qquad (2)$$

Expressing the hydrogen bromide concentration as a molefraction of the bromine concentration, f, equations 1 and 2 may be rewritten

$$dx/dt = k_1 k_3 k_5\ [\text{Olefine}]\ [\text{Bromine}]\ \frac{f}{k_2 k_4 f + k_1 k_5} \qquad (3)$$

$$dx/dt = k_1 k_5\ [\text{Olefine}]\ [\text{Bromine}]\ \frac{f}{k_2 f + k_5}\ [\text{Olefine}]/[\text{Bromine}] \qquad (4)$$

If olefine and bromine concentrations are chosen to be equal and the coefficients of f be unity, both expressions lead to an identical one of the type

$$dx/dt = k'\ [\text{Olefine}]\ [\text{Bromine}]\ \frac{f}{f+1}. \qquad (5)$$

Obviously this assumption cannot be valid in all cases but one may expect that in every instance, a range of catalyst concentration may be found where this holds good. Further, the expression will be reduced to a simple

bimolecular type if $f = \frac{k_1 k_5}{k_1 k_5 - k_2 k_4}$ in equation (3) Equation (4) will be similarly reduced to this type if the reactants are initially at the same concentration and $f = 1/1 - k_3/k_5$ It has been observed that the introduction of activating groups reduces both the period of induction and influence of the catalyst on the rate of the addition reaction ( ). One may expect, therefore, for each olefine three different stages in the catalysed reaction·

1 The reaction is represented by the full rate equation (3).

2 The reaction is represented by the rate equation (5)

3. The reaction gives a bimolecular constant

Evaluation of all the constants in the full rate equation is not feasible with the existing experimental data but the general validity of the concepts may be seen by examining the figures for crotonic acid (Tables II, III and IV)

The three tables present data which correspond to the different stages mentioned in the foregoing para in the order given The experimental work in the earlier parts of this work has shown that though the determining factor

TABLE II

Concentration of Olefine = Concentration of Bromine M/15 , Concentration of Catalyst (HBr) 1·05 moles % of Br

Reaction %	Rate Constant mole/min.$^{-1}$ calculated using Eqn. 5	Rate Constant mols/min^{-1}. Bimolecular
10	2 006	0 0168
15	2 396	0 0195
20	2 865	0 0221
25	3 115	0 0238

TABLE III

Concentration of Olefine = Concentration of Bromine M/15 , Concentration of Catalyst (HBr) 2·10 moles % of Br

Reaction %	Rate Constant using Equation 5 moles/min $^{-1}$	Rate Constant, Bimolecular moles/min $^{-1}$
10	1 31	0·0192
15	1 37	0·0228
20	1·35	0·0260
25	1·34	0·0269

TABLE IV

Concentration of Olefine - Concentration of Bromine M/15, Concentration of Catalyst, (HBr) 6 90 moles % Br

Reaction %	Rate Constant using Equation 5 moles/min $^{-1}$	Rate Constant, Bimolecular moles/min.$^{-1}$
10	1 267	0 0538
15	1·340	0 0552
20	1·422	0 0552
25	1 485	0 0554

Note.—The rate constants in Tables II, III, IV refer to a temperature of 35.5° C

in the reaction is the ratio between the catalyst and bromine, the dual activation of the double bond, *viz.*, the internal group influences and the external catalyst influence, has to be recognised and though equation 5 and the bimolecular equation can both be derived from the simpler set of reaction the more complete one is to be preferred

Since in every case the limiting reaction is a bimolecular one,* the limiting value of the velocity constant will be proportional to $\frac{k_1 k_5}{k_1 k_5 - k_2 k_3}$ Each of these constants being specific for a reaction different catalysts may be expected to lead to different limiting values of the velocity constant. Also, the catalyst-bromine concentration ratio for each of the stages may not be the same. The following data obtained with iodine monochloride as catalyst and crotonic acid as the olefine illustrate this point.

TABLE V

Olefine and Bromine concentrations M/15

Catalyst Concentration	Reaction %	Rate Constant Eqn 5	Rate Constant, Bimolecular
0·95 % Bromine	10	2 407	0·0109
	15	2 891	0 0228
	20	2 981	0 0252
	25	3 134	0 0296
7 80 % Bromine	10	0 8005	0 0521
	15	0 6861	0 0541
	20	0 6434	0 0552
	25	0·5659	0·0545

* Note Robertson and co-workers (*J C S*, 1945, 129 &c) at higher concentrations get the reaction as termolecular. This is considered in a later part.

The applicability of the equation to other compounds and the influence of substituent groups are considered in the next part

SUMMARY

A kinetic equation has been derived for a homogeneous catalysed reaction in which both the reactants of a bimolecular reaction are activated by the catalyst and the equation applied to the reaction between crotonic acid and bromine catalysed by hydrogen bromide The variation of rate with change of catalyst is also indicated

REFERENCES

1 Anantakrishnan and Venkatraman *J C S*, 1939, 224
2 ——— ——— *Chem Reviews*, 1943 33, 52

THE KINETICS OF THE OLEFINE-BROMINE REACTION

Part V. Influence of Substituents on the Applicability of the Kinetic Equation of the Catalysed Reaction

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In Part I of this series it was observed that the induction period and the minimum concentration of catalyst needed to eliminate this varied with the olefine and a hypothetical curve was drawn correlating these [1] The kinetic equation derived in Part IV (preceding paper) must be consistent with this observation if it is to be a general one Two similarly substituted trans ethylene derivatives were chosen for this study, fumaric acid and stilbene The choice of these was determined by the following considerations In dealing with a reaction involving the polarisability of the double bond, the complication of dipole moment influence has to be minimised and symmetrically substituted trans compounds present the obvious choice. An increase in the number of activating groups attached to the doubly bound carbon leads to a very fast reaction which renders accurate experimental work difficult with available equipment Alpha-beta unsaturated acids have been shown by Kharasch[2] to be free from the complication of a peroxide effect Phenyl ethylene reacts faster than ethylene but one may expect the symmetrical diphenyl ethylene to be less reactive through the opposing influences of the phenyl groups The deactivation, however, cannot be as great as with the two carboxyl groups. Combining with the earlier observations, it was expected that a more exact correlation between activation and catalytic influence could be obtained The results of the kinetic investigations are given below (Figs 1 and 2) (Tables I, II, III, IV, V and VI).

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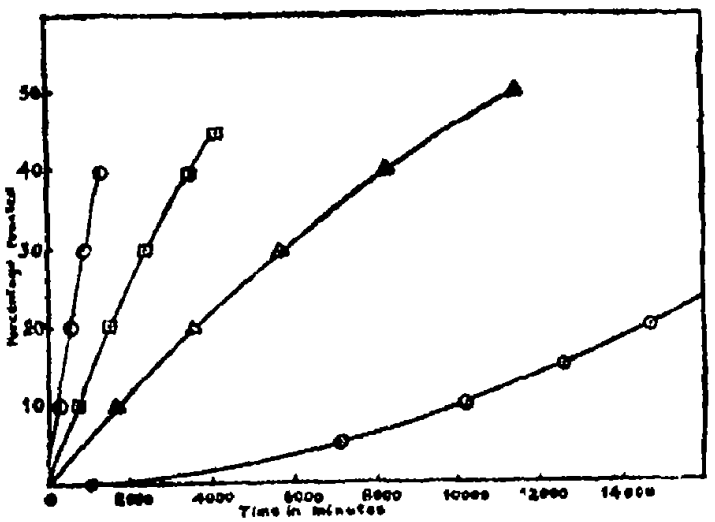


FIG. 1.

I. Uncatalyed Reaction.
II, III, IV Catalysed reactions at 35° 5 C., 43° 5 C. and 50° 6 C

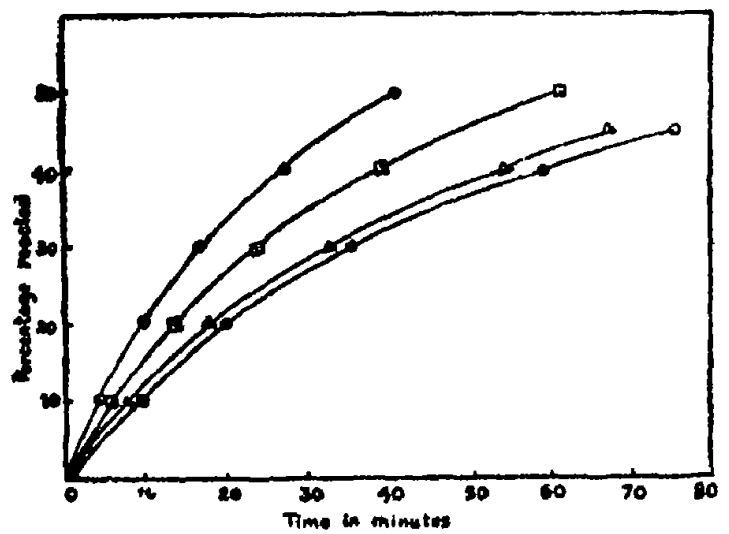


FIG. 2

I. Uncatalysed Reaction.
II, III, IV. Catalysed reactions at 35° 5 C, 43° C and 50°·55 C

TABLE I

Concentration of Fumaric acid*, Concentration of Bromine M/30, Concentration of Hydrogen Bromide 11 01 moles % of Bromine, Temperature of reaction : 35°·5 C

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant "Bimolecular"
5	852	0 0189	0 00185
10	1698	0 0194	0·00196
15	2604	0 0193	0 00203
20	3576	0 0194	0 00210
25	4596	0 0191	0 00217

* *Note* —After writing up this paper, the authors came across the work of P W Robertson *et al* in which fumaric acid happens to be one of the compounds studied The bearing of that on the present work will be considered in a later communication

TABLE II

Concentration of Fumaric acid, Concentration of Bromine M/30, Concentration of Hydrogen Bromide 11 01 moles % of Bromine, Temperature of reaction 43° C

Reaction %	Time in minutes	Rate Constant Eqn 5 (Part IV)	Rate Constant "Bimolecular"
5	344	0 0450	0 00459
10	712	0·0450	0·00468
15	1100	0 0453	0 00481
20	1512	0·0453	0 00495
25	1956	0 0452	0 00512

TABLE III

Concentration of Fumaric acid, Concentration of Bromine M/30, Concentration of Hydrogen Bromide 11 01 moles % of Bromine, Temperature 50° 6 C

Reaction %	Time in minutes	Rate Constant Eqn 5 (Part IV)	Rate Constant "Bimolecular"
5	134	0 117	0 0118
10	274	0·116	0 0122
15	427	0 112	0·0124
20	598	0 107	0·0126
25	790	0 109	0·0127

The thermal reaction between Stilbene and Bromine is a fast one and it was found that a concentration of M/30 the reaction was completed in less than half an hour To bring the speed of the reaction within measurable control, it was found necessary to work with concentrations of M/600

TABLE IV

Concentration of Trans-Stilbene ; Concentration of Bromine M/600 , Concentration of Hydrogen Bromide 11 01 moles % Bromine ; Temperature 35° 5 C.

Reaction %	Time in minutes	Rate Constant Eqn 5 (Part IV)	Rate Constant " Bimolecular "
5	3 8	8 12	8 21
10	7 9	7·74	8 44
15	12 6	6 91	8·40
20	18 4	6 36	8 15
25	24 8	5 84	8 06
30	32·7		7 87

TABLE V

Concentration of Stilbene , Concentration of Bromine M/600 , Concentration of Hydrogen Bromide 11·01 % of Bromine

Temperature	43°·0 C		50° 55 C	
Reaction %	Time in minutes	Rate Constant " Bimolecular "	Time in minutes	Rate Constant " Bimolecular "
5	2 9	10 89	2 1	15·04
10	6 1	10 93	4 35	15 33
15	9 7	10 89	6 95	15·24
20	13 9	10 79	9 95	15 08
25	18·5	10 81	13 10	15 26
30	23 8	10 80	16 95	15 17

TABLE VI

(All values refer to 35 5 C.)

Reacting Olefine	Concentration Moles/litre	Induction Period in minutes	" Velocity Constant " mol /litre, min.$^{-1}$
Crotonic acid ..	M/30	25	0 038
Tiglic acid	,	4	0 20
Dimethylacrylic acid	,	1 2	0 78
Fumaric acid	,,	1062 0	0 0020
Allyl Chloride .	M/300	Less than 2	1 22
,, Bromide	,	2 5	0·72
Stilbene ..	,,	Ca 3 8	0·40 (estimated) by extrapolation

It will be noticed that fumaric acid gives a reasonable " bimolecular " constant only at about 50° C even though the proportion of catalyst is the same as that used in earlier experiments. On the other hand, stilbene at 35·5 can be considered to behave equally well by the use of Equation 5 or

the bimolecular rate equation and at higher temperatures gives a good bimolecular constant Qualitatively, therefore, one may conclude that the minimum concentration of the catalyst required for giving a " bimolecular " constant is greater in the case of an olefine with deactivating groups than that of one with activating groups, the limiting value being reached earlier in the latter case.

To get a better picture of the role of activating groups, one can compare the limiting value of the constants where possible with the induction periods observed or what probably amounts to the same thing, with the minimum concentration of catalyst required to give a bimolecular constant

If one were to plot the values of the " velocity constant " at comparable concentrations against the induction periods, a curve asymptotic towards both axes can be obtained but the experimental values for the purpose has still to be obtained. The figures in the table (Table VI), however, clearly show the trend expected

One may then justifiably consider that the rate equation derived in the previous part (IV) fits in with the behaviour of both structural influences and catalytic influences.

In Part I of this series[8] it was observed that the experimental observations of Williams[7] on the addition of bromine to ethylene in carbon tetrachloride solution showed the characteristics of a chain reaction and that the per cent. reaction-time curve could be represented by the relation of the type:

$$x = \frac{100}{1 + e^{-\phi\theta}}$$

It was anticipated then that in the non-polar solvent there is a likelihood of a heterogeneous reaction complicating the interpretation The recent observations of Robertson and co-workers appears to indicate the presence of a definite heterogeneous reaction in this solvent All observations in acetic acid, however, indicate that the reaction in this polar solvent is definitely homogeneous. While the polar solvent can function as an activating medium for the reaction, in the case of olefines where deactivating groups are present and where the concentration of the added external catalyst is not adequate, the competition between the acetanion and the bromide ion in the latter steps in the reaction may slow down the rate and the reaction-time curve simulates one of a degenerate branching chain. This anticipation is borne out by the uncatalysed addition to fumaric acid at 35° C. (Fig. 3).

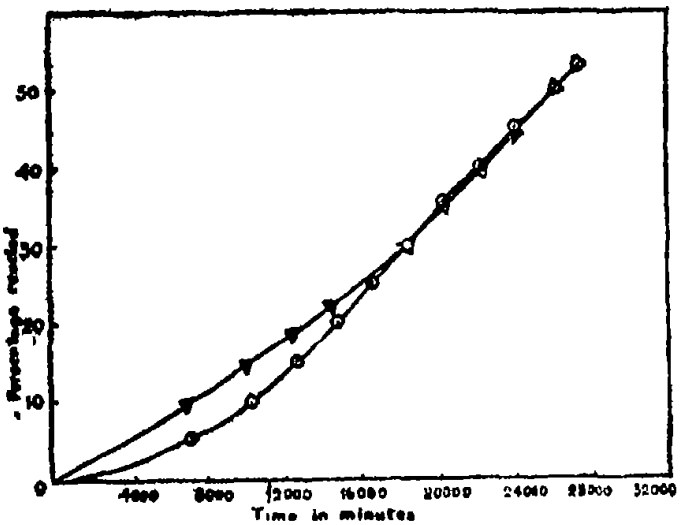


FIG 3

I. Theoretical. II Experimental

Strict conformity between the theoretical and experimental values may not be expected in the initial stages of chain development but the coincidence is nonetheless striking. The maximum value of the reaction rate is reached when about 50% of the reaction is over, again, conforming to Semenoff's generalisations on degenerate branching chains.[6] It is expected that further work in progress will reveal other similar instances

A word of explanation is necessary for the choice of an aryl ethylene in the investigation Competition experiments had shown[2] that the introduction of the phenyl nucleus activates the double bond. From the genesis of the T-effect, that the location of two groups of this class of substituents may be expected to neutralise each other's influence, especially if the trans form were chosen Unpublished observations of one of us in the competition experiments (S V A) indicated that this does not take place. The present investigations also show that the double bond is definitely activated even with two phenyl groups symmetrically located

EXPERIMENTAL

The reaction velocities were measured by the usual methods as described in Part I, the same accuracy in thermostat control being maintained. Bromine was prepared by the method described by Anantakrishnan and Ingold[8] and its purity tested by the criterion indicated by one of us.[3] Pure Fumaric acid (Kahlbaum's) was repeatedly recrystallised from alcohol to

constant melting point 290° C in a sealed tube. The substance was stored in a vacuum desiccator till used

Stilbene was prepared from benzoin by the method of Ballard and Dehn[4] and the pure trans form used in the investigation.

Summary

A study of the reaction between bromine and fumaric acid and bromine and stilbene brought out clearly the validity of the rate equation derived in the previous part The uncatalysed addition reaction of fumaric acid exhibits the characteristics of a degenerate branching chain.

References

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2	——— and Ingold, C K	*J C S*, 1935, 984
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4	Ballard and Dehn	*J A C S*, 1932, **54**, 3969
5	Robertson and co-workers	*J C S*, 1937, 335, 1938, 182, 1945, 129 &c
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7	Williams	*J C S*, 1932, 979
8	Kharasch and Mayo	*J A C S*., 1933, **55**, 2368

KINETICS OF THE OLEFINE-BROMINE REACTION

Part VI. Further Consideration of the Arrhenius Parameters

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It is well known that in the treatment of any kinetic problem the activation energy is a factor of fundamental importance In any reacting system, the reactants and products represent states of minimum potential energy, while the transition state must be a maximum in between these limits of minima. The reaction involves the breaking of bonds and the formation of new ones and the work done in the process constitutes the activation energy When the reaction of a series of similar compounds are studied, the principal difference that may be expected is in the activation energy. One cannot, however, consider the variation in the other Arrhenius parameter negligible as has been demonstrated by the work of Hinshelwood and co-workers [5, 7, 8]

Though the number of compounds investigated in the present series is as yet small, one has still to consider these parameters as the influence of substituent groups on these is of considerable diagnostic value and is of greater significance than any measurement of velocity constants at a single temperature Since the reaction in question involves the change of a double bond to a single one, rupture of the bond between the atoms of the bromine molecule and the formation of carbon-bromine bonds, one may expect a more or less constant frequency factor† while the activation energy shows systematic variations. The results of evaluating these and the Log $k/1/T$ curve used for the purpose are given below in Table I and Fig. 1.

An examination of both the figure and the table clearly shows that substituents alter both the energy of activation and the frequency factor The activation energy in its turn can be further analysed into the bond energy

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† The quantity of the Arrhenius equation which is approximately kT/h and hence has the dimensions of frequency This term is preferred to the older 'probability factor'.

TABLE 1

Substance	Concentration in moles/l	Temperature °C.	100 k_2 moles/l min $^{-1}$	E Calories	PZ $\times 10^{-5}$
Crotonic acid (*trans*) ..	M/15	25·15	4 360	less than 3000	
		35 40	7 169		
		42 50	10·30	10,800	1·052×10 at 35 5° C
		49·95	15 12		
	M/30	25·15	2 213		
		35 40	3·787		
		42 50	5 860	10,800	19 52 at 35 5° C
		49 95	8·523		
Tiglic acid ..	M/15	30·20	40 15		
		35 50	49 99		
		42 25	62·09	6 800	0·136 at 35 5° C.
		50·05	78 94		
	M/30	30 10	16 66		
		35 50	19 95		
		42 25	24·35	6·800	0·136 at 35 5° C
		50 05	31 52		
$\beta\beta$ Dimethyl acrylic acid	M/30	35 5	77 80		
		42·6	91 66	4·500	
		50 3	108·4		
	M/60	35·5	33 94		
		42·6	42·02	7,200	0·443 at 35·5° C.
		50 3	53 57		
Fumaric acid ..	M/30	35·50	0·2097		
		43·30	0·4950	21,270	2 66×10^7 at 35 5° C
		50 60	1·254		
Stilbene (trans) ..	M/600	35·50	81 5		
		43·30	107 9	7,700	1·995 at 35·5° C
		50 6	150 8		

Key to numbers. 1 Crotonic acid 2 Tiglic acid 3 Dimethyl acrylic acid 4 Fumaric acid, 5 Stilbene.

and repulsion energy and substituents can alter either or both of these. Hinshelwood, Laidler and Timm[8] from a study of the same reaction in a series of aromatic compounds find that the changes occur only in the bond energy. A difference may, however, arise in the present type of reaction arising primarily from the nature of the olefin.

The ground state of an olefine results from resonance among the structures



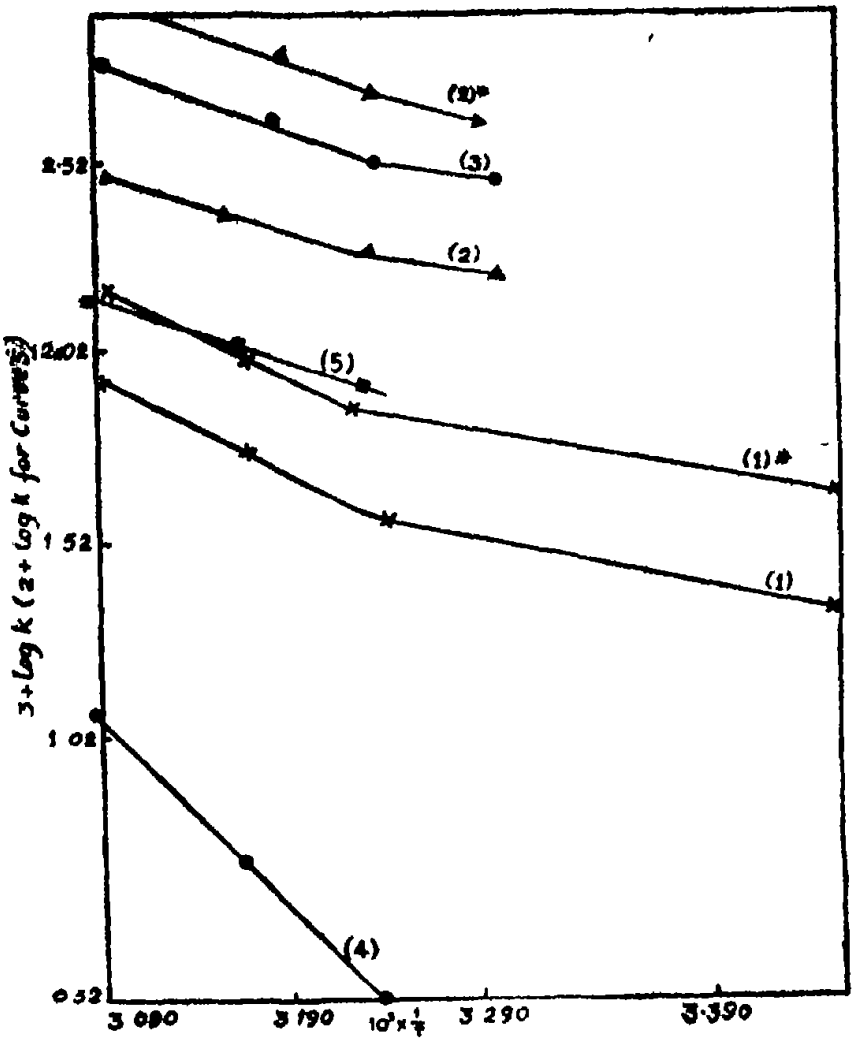


FIG. 1 log k/1/T curve

and forms ψ_2 and ψ_3 will have identical energies only in the case of symmetrically substituted olefines Additive reactivity depends primarily on the opening up of the double bond and will naturally depend on the relative contribution of the different structures which in its turn determines the bond energy as well as the repulsion energy With unsymmetrically substituted olefines the contribution by the ionic structures can be quite appreciable and when this is combined with the presence of groups that facilitate reaction with electrophilic reagents on account of their influence on the state of polarisation of the molecule, the activation energy can be substantially

lower than that for the unsubstituted ethylene No experimental data is available at present for the activation energy, for the reaction between ethylene and bromine but Sherman[13] using Eyring's method[8] has evaluated by using the transition state method that this has a value of about 23 Kcal The expectation is substantiated by our values for the monobasic acids studied. A similar reduction in activation energy can be expected with substituents of Class 7 ($\pm$ T)[9] which can stabilise the carbonium ion of the first stage of bromine addition even if symmetrical disubstituted compounds are considered. The results with stilbene clearly bears this out.

On the other hand with deactivating groups, an increase in the activation energy is offset by the resonance energy, so that even with symmetrical disubstitution products like fumaric acid, the observed energy of activation is not far from the calculated value for ethylene itself

A close examination of the log k — 1/T curve of the first three compounds in the table reveals a definite change of slope below 25° C , indicating that the reaction is a composite one [6] The very low value for the activation energy in the lower temperature region suggests a termolecular reaction changing over to a bimolecular one at the higher temperatures. This feature appears to be independent of concentration changes as may be noticed from the fact that this results only in a parallel shift of the log k — 1/T curve. (Starred figures in the figure refer to higher concentrations) The observations of Robertson and co-workers[12] with a number of olefines at 25° C. then becomes quite understandable Considerable variations in rate constants can be accounted for solely by changes in activation energy but our present data are inadequate for a complete analysis Mention should, however, be made here of the pronounced catalytic effect of hydrogen halides (or more accurately by hydrogen ions) The calculations of Polanyi[10, 11] have shown that the proton affinity of ethylene is of the same order of magnitude as that of water and as such association of a proton prior to the addition reaction can be expected to facilitate the change by providing a seat of attack. A corollary to this one has to expect that attack by nucleophilic bromine will not be facilitated by the same catalyst

Turning now to the other parameter, namely, the frequency factor, a normal second order reaction requires a value of the order of 10^9 while the values in the table show considerable variations from this. A point of particular interest is the fact that fumaric acid appears to react much faster than it should (a bimolecular reaction with an activation energy of 20 Kcal, should give a rate constant of the order of 10^{-12} with a frequency factor of normal value but observed values are much higher. The remaining four

compounds react with bromine at rates that bring them under the category of "slow" reactions. This is only to be expected when one considers the nature of the reaction. For the reaction to take place, encounters have to be made between molecules possessing the requisite activation energy. Secondly, the initiation of attack is by an electrophilic reagent. Further, the encounter between the reactants must be in the right phase in the region of the double bond. As a first approximation, one can consider that the ratio of the number of effective collisions, z^*, to the total number of collisions calculated in the usual manner, z, will be proportional to the area of the strip cut on the spheroid of the dimensions of the molecule by two parallel planes perpendicular to the direction of the reacting bond, a_s, to the total area of the surface of the spheroid, a. Taking the surfaces as functions of the square of bond distance r_b and major axis of the ellipse r_m, we have

Taking into account the fact that the rate determining step in the reaction involves only one of the two doubly bound carbon atoms, this ratio should be halved in the present case All the compounds studied here have major axes of the order of 6 — 11 Å while the carbon-carbon double bond distance is only 1·33 Å. As a consequence, the frequency factor may be expected to be reduced from 10^9 to about 10^8, a value not far from the ones obtained.†

A further complication that one has to consider in the study of unsaturated compounds of the polysubstituted olefine group is the isomerisation of *trans* compounds to the *cis* form. This complication is absent only in the case of $\beta\beta$-dimethylacrylic acid in the present series. Unpublished observations of the authors indicate that *cis* crotonic acid is less reactive than the *trans* while maleic acid is considerably more reactive than fumaric acid. It is well known that halogens facilitate the interconversion of these stereoisomeric forms[8, 10] and this can easily account for the observed anomalies in the frequency factor. Another contributory cause for reduction in the frequency factor is the composite nature of the reaction

In a number of reactions, a close correlation is observed between log PZ and $1/E^{\frac{1}{2}(5)}$ and a similar relationship may be looked for in the present reaction also. For the sake of comparison the product of these two quantities has been taken for Table II.

† A more rigorous analysis of this and other "slow" reactions will be communicated shortly.

TABLE II

Substance	Log PZ × 1 /E
Crotonic acid ..	0·056
Tiglic acid ..	0·046
Dimethylacrylic acid ..	0·047
Fumaric acid ..	0·011
Stilbene	0·050

It will be observed that the product is constant within the limits of experimental error, the exception being provided by fumaric acid The significance of this can be considered only after a fuller investigation.

SUMMARY

An analysis of the Arrhenius parameters for the addition reaction indicates that the reaction is a composite one and of the "slow" type The influence of substituents on the energy of activation and on the frequency factor is discussed and the abnormal values of the latter are accounted for A close correlation is also noticed between the two

One of the authors (R V) thanks the authorities of the Annamalai University for giving the necessary facilities for experimental work.

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CHEMICAL EXAMINATION OF THE BARK OF *ALANGIUM LAMARKII* THWAITES. ISOLATION OF THE ALKALOID ALANGINE

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Alangium Lamarkii or Ankula as it is known in Bengali and Sanskrit, and Akola in Hindi, is a small handsome evergreen tree belonging to the Natural Order of Alangiaceæ It is met with throughout India, often growing wild, but sometimes cultivated as an ornamental garden plant for the beautiful, narrow, oblong and prominently reticulated leaves and white wax-like glossy flowers It is particularly abundant in Chota Nagpur, Orissa, Andhra districts, Central Provinces, United Provinces and South-Eastern Punjab.

The plant is highly medicinal. According to Kirtikar and Basu,[1] the root is acrid, bitter, slightly pungent, heating, anthelmintic, alterative It cures erysipelas, biliousness, inflammations and snake bites and acts like a fish poison. The bark is emetic, alexipharmic and cures cough, rheumatism, pain, inflammations, biliousness, diseases of the blood, hydrophobia, rat-bite, lumbago, dysentery, diarrhœa and worms. The seeds are cooling, aphrodisiac, indigestible, tonic, nutritive and laxative They cure burning sensations, consumption, hæmorrhage, biliousness, erysipelas, cough and loss of appetite. They have also a reputation in the cure of leprosy.

The seeds of the plant have already been worked out by Bhargava and Dutt,[2] who isolated from them an interesting sterol having a molecular formula $C_{43}H_{64}O_7$, which they named 'alangol'. Very little fixed oil was found in the seed and no other constituent could be detected

The bark of the plant has not yet been properly worked by anyone. Dymock[3] has reported the presence of an uncrystallisable alkaloid which could not be obtained in a pure form According to him all the salts of the base are uncrystallisable. On ignition, the platinum salt gave 20 70% of platinum from which the molecular weight of the base was found to be 265·9. No further work has been done by any one on this subject.

The present authors working on the bark of the plant have been able to isolate an alkaloid crystallising in glistening, yellow prisms and melting at

205-08° C The molecular formula of the substance which has been named 'alangine' was found to be $C_{19}H_{23}O_2N$, and it behaved like a mono-acid base with one methoxy group. There was an indication of an alcoholic hydroxy group due to the formation of acetyl and benzoyl derivatives, but they did not give good analytical results.

Alangine is strongly basic in nature and forms well-defined and crystalline hydrochloride, iodide, oxalate, tartrate, nitrosate and iodomethylate It is a tertiary base but does not contain any $>N-CH_3$ group as by Herzig and Meyer's method no indication of such a group in the molecule was obtained.

Alangine is present in the bark of *Alangium Lamarkii* to the extent of 0·1%. The bark besides containing alangine also contains a fair proportion of colouring matters, potassium nitrate, gum, etc Fresh bark has been found to contain a greater proportion of alangine than the bark which has been stored for some time. The chemical properties and reactions of alangine correspond to no known alkaloid. So it must be a new compound.

Experimental

Extraction of the bark with different solvents

20 gm. of the finely powdered bark were extracted with different solvents in a Soxhlet's apparatus, the solvent evaporated and the residue dried to a constant weight The percentage of the extract by each solvent is given below :—

Water	15·05
Alcohol	13·98
Acetone	8 22
Chloroform	2·96
Ethyl acetate	3 01
Benzene	1·15

In each of the above extracts the reactions of an alkaloid was given by all the alkaloid reagents. The extracts were also extremely bitter in taste

Isolation of the alkaloid

200 gm of the air-dried powdered bark were repeatedly percolated with acidulated water (0·5% HCl) at the ordinary temperature until the last extract obtained did not give any appreciable precipitate with Dragendorff's reagent. The extract gave the following reactions with various alkaloid reagents :—

(1) Dragendorff's reagent	..	Thick orange precipitate.
(2) Wagner's reagent	..	Thick brown precipitate
(3) Meyer's reagent	..	Deep yellow precipitate.
(4) Phosphotungstic acid	..	Bright yellow precipitate.
(5) Phosphomolybdic acid	..	Thick yellow precipitate
(6) Platinic chloride	..	Yellow precipitate.
(7) Auric chloride ..	..	Yellow precipitate.
(8) Tannic acid .	.	Buff coloured precipitate.
(9) Picric acid ..	..	Yellow crystalline precipitate.
(10) Chromic acid .	..	Yellow-brown precipitate
(11) Sodium carbonate	..	Yellow precipitate (Free alkaloid).
(12) Conc. Sulphuric acid	..	Light brown colouration.
(13) Luchini's reagent	..	Yellow-brown-violet-green.
(14) Erdmann's reagent	..	Violet-orange.
(15) Conc. Nitric acid	..	Light violet.
(16) Frode's reagent ..	..	Violet, changing to yellow.

The total extract was neutralised with dilute sodium carbonate and the resultant thick yellow precipitate filtered off, washed with water and dried in the air. It was then extracted with hot ammoniated alcohol (0·5%) and the extract after neutralisation with acetic acid, evaporated to a syrup under reduced pressure The syrupy material was then extracted with ethyl acetate, and the ethyl acetate extract after concentration, precipitated with a mixture of ether and petroleum ether (2 · 1) The resulting granular yellow precipitate was filtered off, washed with petroleum ether and then further purified by repeatedly dissolving it in chloroform and reprecipitating with ether The purified alkaloid which was thus obtained as a bright yellow powder was finally crystallised from a mixture of chloroform and ether and the process repeated a number of times until no further rise in the melting point was noticed. The base was thus obtained in the form of glistening yellow elongated prisms melting at 205–08° C. with decomposition

It is sparingly soluble in cold water but more so in the hot. It is easily soluble in alcohol, ethylacetate, acetone, chloroform, carbon disulphide and pyridine but is quite insoluble in benzene, ether and petroleum ether. An aqueous solution of the alkaloid is extremely bitter to taste and is faintly basic towards litmus, phenolphthalein and methyl-orange. The substance is optically active, showing $[\alpha]_D^{28°} = +9°$ in alcohol. A microphotograph of the alkaloid is given showing its finely crystalline form. Found: C =

75·92, 76·02%; H = 8 54, 8·48%; N = 4·75, 4·82% (Duma's); 4·47, 5 04% (Kjeldahl); M.W. = 296,304,297 (Rast's Camphor method); 307,297 (Ebullioscopic in Chloroform); 297·6, 292·3 (ignition of the chloroplatinate); 290·6, 304·0 (ignition of the Chloroaurate); $C_{19}H_{25}O_2N$ requires C = 76 25%, H = 8·36%, N = 4·68%; M.W. = 299

The alkaloid contains one methoxyl group in the molecule. (Found: OCH_3 = 10·45, 10 25, 10 42 by Zeissel's method $C_{18}H_{23}ON$ OCH_3 requires OCH_3 = 10·36%.) The absence of N-methyl was confirmed.

Preparation of the salts of the alkaloid

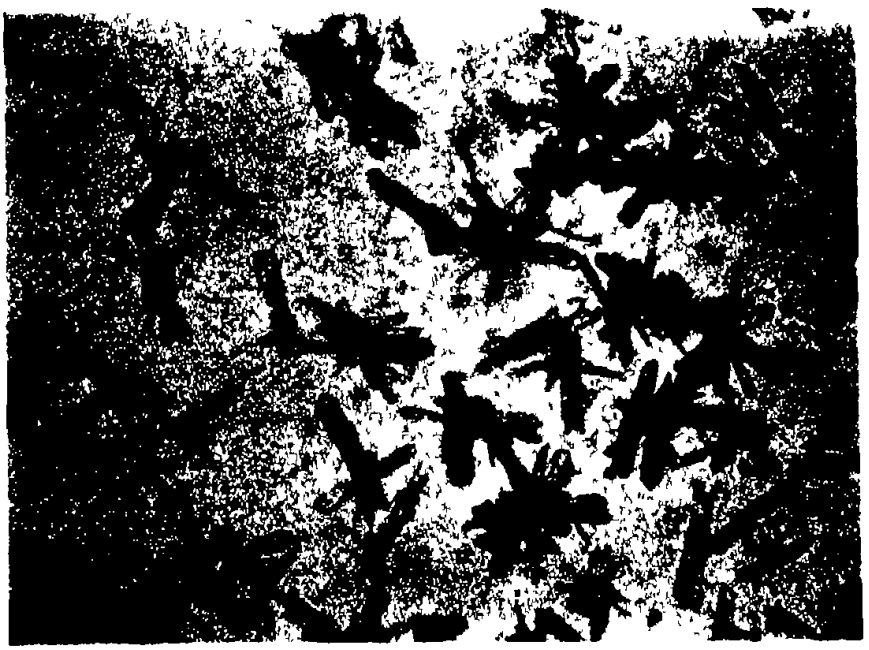
Alangine hydrochloride.—The hydrochloride of the base was prepared by dissolving it in alcohol and treating with a slight excess of warm alcoholic hydrogen chloride On cooling and adding a little ether to the solution, the hydrochloride was obtained as yellow crystalline prisms, melting at 264° C It is easily soluble in water and ordinary organic solvents except benzene, ether and petroleum ether. (Found: Cl = 9·94; $C_{19}H_{25}O_2N$ HCl requires Cl = 10·58 per cent.)

Alangine sulphate—This was obtained by adding alcoholic sulphuric acid to an alcoholic solution of the base, and diluting the mother-liquor slightly with ether. The sulphate came down as a light yellow powder melting at 118° C. The salt is sparingly soluble in cold water but is readily soluble in alcohol, chloroform and acetone. It is insoluble in ether, benzene and petroleum ether. (Found: S = 4·59, 4 71; $(C_{19}H_{25}O_2N)_2H_2SO_4$ requires S = 4·60%)

Alangine nitrate.—This was obtained in a similar way as the hydrochloride and the sulphate, from alangine and alcoholic nitric acid It is a yellow crystalline powder melting at 176° C. The properties of this substance are similar to those of the other inorganic salts.

Alangine iodide—To a hot aqueous solution of the chloride was added a concentrated solution of potassium iodide The iodide separated as a deep yellow crystalline precipitate. It was recrystallised from ether-alcohol mixture in the form of yellow prisms melting at 178° C with decomposition The substance is sparingly soluble in water but readily in alcohol. It is insoluble in ether and petrol ether. (Found: I = 29·38; $C_{19}H_{25}O_2N$ HI requires I = 29·74%.)

Alangine acetate, tartrate and oxalate.—These were prepared by the action of alcoholic acetic, tartaric and oxalic acids on alcoholic solutions of alangine. They are all yellow, crystalline substances with properties



similar to those of the chloride. Alangine acetate melts at 202° C, tartrate at 220° C. and oxalate at 89° C.

Alangine picrate.—To a solution of the base in dilute hydrochloric acid was added a saturated aqueous solution of picric acid when a light-yellow, crystalline powder came down This was recrystallised from ether-alcohol mixture in glistening flakes, melting at 84° C. It is soluble in alcohol, chloroform, ethyl acetate and acetone and sparingly in benzene. It is insoluble in ether and petrol ether. (Found: N = 10·34, $C_{28}H_{30}O_9N_4$ requires N = 10·60%.)

Alangine-iodomethylate — To a solution of the base (1 gm) in chloroform (3 c c), methyl iodide (1 c c) was added and the mixture strongly cooled On allowing to stand for about two hours, a deep yellow crystalline substance separated out This was filtered, washed with chloroform and dried under vacuum at room temperature (21° C) It melts at 201° C with decomposition. (Found. I = 28·53; $C_{30}H_{33}O_2NI$ requires I = 28·79%.)

The quaternary salt is very soluble in water and alcohol, but the solubility decreased in the order—ethyl acetate, chloroform, acetone and benzene. It is completely insoluble in ether and petrol ether.

Summary and Conclusion

1. From the bark of *Alangium Lamarkii* Thwaites, a new alkaloid has been obtained crystallising in long yellow glistening prisms, m p 205—08° C The molecular formula of the alkaloid has been found to be This has been named "Alangine"

2. The alkaloid has been found to be a monoacid base containing one methoxy group but no $>N-CH_3$ group.

3. The alkaloid which is dextrorotatory easily gives crystalline salts with organic and inorganic acids and the hydrochloride, sulphate, nitrate, iodide, acetate, tartrate, oxalate, picrate and iodomethylate have been prepared and described

References

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COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE METALLIC DERIVATIVES OF ISONITROSODIPHENYL-THIOBARBITURIC ACID

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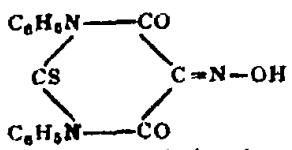
Violuric acid and its highly coloured organic and inorganic salts have been investigated from the point of view of colour in relation to chemical constitution by a large number of workers. Hartley,[1] Hantzsch,[2] Meek and Watson[3] have shown that the greater the basic character of the base, the greater is the intensity of the colour of the salt formed

The next interesting work in this connection was done by Lal and Dutt[4] who took up the study of isonitrosothiobarbituric acid or thioviolurie acid which was prepared by them for the first time by the action of nitrous acid on thiobarbituric acid. The alkali and organic salts of this compound were found to be highly coloured substances, far more so than the corresponding salts of violuric acid, which was due to the introduction of a sulphur atom in place of an oxygen atom. The effect of sulphur on the colour of the organic compounds and dyestuffs was previously noticed by Purvis, Jones and Tasker,[5] who noticed that the thio-oxalates of alkalies are yellow in colour whereas the corresponding oxalates are colourless. Further Lal and Dutt examined the absorption spectra of thioviolurates and also the dissociation constants of a number of them which were soluble in water, but on comparing the results thus obtained, they came to the conclusion that the colour of thioviolurates is not intimately connected with electrolytic dissociation and in fact, intense colours were possessed by compounds which were altogether insoluble in water or hydroxylic solvents and whose absorption spectra had to be determined in acetone or chloroform solutions.

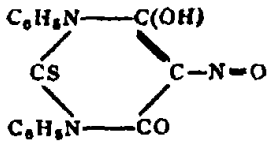
As a result of the work of Lal and Dutt on thiovioluric acid, Prakash and Dutt[6] thought that any further loading of the molecule of violuric acid by heavy substituents might lead to further accentuation of colour. They prepared sym-diphenyl-violuric acid and showed that the organic salts derived from weak bases like pyridine and aniline have colours no less intense than the alkali salts. The possibility of molecular ionisation having

been ruled out, the most reasonable explanation of the origin of colour in these compounds was thought to lie in a fundamental change in the constitution of the molecule on salt formation in accordance with the theory of colour on the basis of molecular strain advanced by Dutt.[7, 8]

The present authors prepared the inorganic salts of diphenyl-thioviolurie acid and found accentuation of colour in accordance with the above theory. The deepening of colour during salt formation lies in a change in the structure of the molecular from the oximino-ketonic to the nitroso-enolic form which is more strained according to the theory of colour on the basis of molecular strain, advanced by Dutt. The organic salts of diphenyl-thioviolurie acid have already been worked by Dass and Dutt.[9]



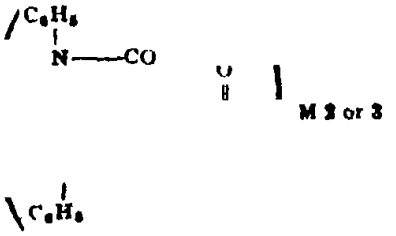
"Oximino ketonic form"



"Nitroso-enolic form"

Theoretical considerations show that the metallic salts of diphenyl-thioviolurie acid are probably of the nature of internally complex compounds. The acid molecule in its nitrosoenolic form contains one replaceable hydrogen which is replaced by the metal atom during salt formation.

The possibility of inner complex salt formation arises wherever acidic and donor functions (such as amino, carbonyl, etc., groups) are suitably placed in the same molecule, *i.e.*, in 1:4 or 1:5 position to one another. This is the case with diphenyl-thio-violuric acid where nitrogen atom of the nitroso group can act as a donor and bring about ring-formation Their stability, low melting points, solubility in organic solvents also support the view that they are inner complex salts. The salts of bi and trivalent metals may be given the following general formulæ where M is the metal atom:—



Experimental

Preparation of diphenylthioviolurie acid.—A mixture of thiocarbanilide (10 gm.), malonic acid (6 gm.) and acetyl chloride (9 c.c.) was heated on a

TABLE I. *Properties of Salts*

	Name of the metal	Colour in solid state	Colour in acetone	M.P. °C	Absorption maxima A°
1	Silver ..	Light Green	Green	216	..
2	Lead ..	Light Brown	Brown	200	5050
3	Mercuric ..	Green	Greenish Yellow	225	7200
4	Bismuth	Orange Brown	..	201	4850
5	Copper .	Brown	Light Brown	224	5250
6	Cadmium ..	Brown	Reddish Brown	256	..
7	Antimony ..	Orange	Yellowish Orange	218	5200
8	Tin	Brick Red	Light Red	..	..
9	Ferrous .	Deep Blue	Deep Blue	220	6650
10	Ferric	Dark Green	Green	210	6520
11	Aluminium ..	Buff Coloured	Buff	212	4680
12	Chromium ..	Green	Green	211	5320
13	Cobalt ..	Dark Brown	Dark Brown	255	5720
14	Nickel .	Yellowish Brown	Yellowish Brown	315	5600
15	Manganese ..	Slate Coloured	Blue (Light)	295	4980
16	Zinc .	Light Brown	Brown	264	4850
17	Calcium .	Light Pink	Almost Insoluble	above	5080
18	Strontium	Pink	Pink with Blue tinge	350°	5120
19	Barium .	Dark Pink	.	..	5150
20	Magnesium	Light Brown	Light Brown	.	4830
21	Cerium ..	Pale Yellow	Pale Yellow	230	4870
22	Gold .	Dark Brown	Brown	200	5150
23	Platinum ..	Buff Coloured	Light Brown	204	4750
24	Uranium .	Reddish Brown	Reddish Brown	219	..
25	Ammonium	Bluish Grey	Greenish Blue	213	6060
26	Potassium ..	Deep Emerald Green	Brilliant Green	219	6560
27	Sodium ..	Greenish Black	Intense Emerald Green	128	6610

Estimation of Metal and Sulphur

	Metallic salt	% of metal observed	Theoretical % of Metal	Ratio of Metal to Acid	% of Sulphur observed	Theoretical
1	Sodium .	..	.	.	9·39	9·22
2	Potassium .	..	.	.	8·84	8·81
3	Ammonium .	..	..	..	9 86	9·35
4	Silver	24 93	24 97	1 : 1	7·28	7·43
5	Ferrous ..	7 87	7 93	1 : 2	9·04	9·11
6	Ferric ..	5 46	5·43	1 : 3	9 28	9·36
7	Aluminium ..	2 68	2·70	1 : 3	9·75	9·65
8	Chromium .	5·10	5 01	1 : 3	9·37	9·40
9	Nickel ..	8 27	8·30	1 : 2	9·00	9·07
10	Copper .	8·89	8·93	1 : 2	9·11	9·01
11	Cobalt ..	8·30	8 34	1 : 2	9·16	9·07
12	Magnesium ..	3 55	3·62	1 : 2	9·42	9·53
13	Calcium .	7·54	7·61	2 : 3	6·01	9·14
14	Strontium ..	15·16	15·29	2 : 3	8·30	8 38
15	Barium ..	22 17	22 05	2 : 3	7 81	7·71
16	Lead .	24·20	24·23	1 : 2	7·45	7·50
17	Antimony ..	10 97	11·13	1 : 3	8·70	8·80
18	Bismuth ..	17 62	17·70	1 : 3	8 09	8·14
19	Zinc ..	9 10	9·16	1 : 2	9·00	8 98
20	Cadmium ..	14·67	14·78	1 : 2	8·49	8·43
21	Mercuric ..	23·10	23·64	1 : 2	7·46	7·55
22	Manganese ..	7·60	7·81	1 : 2	9·13	9·12
23	Gold ..	16·24	16·56	1 : 3	8·26	8·22
24	Cerium .	9·62	9·77	1 : 4	8·74	8·69
25	Platinum ..	22·90	23·15	1 : 2	7·29	7·60
26	Uranium ..	26·01	26·77	1 : 2	6·98	7·23

water-bath under reflux for about half an hour. The solid yellow mass was broken up, ground with water in a mortar, filtered, washed, dried and crystallised from glacial acetic acid when yellow needles of m p. 245° C were obtained.

Diphenyl-thiobarbituric acid as obtained above (20 gm) was dissolved in KOH solution (5%) and a solution of sodium nitrite (20 gm) in minimum quantity of water was added The mixture was filtered, cooled in ice and gradually acidified with ice-cold dilute sulphuric acid The light buff-coloured precipitate was allowed to stand overnight, filtered, washed with water and dried and crystallised from boiling glacial acetic acid when it was obtained in glistening prisms melting at 227° C

Preparation of the metallic salts.—The ammonium salt was prepared by adding concentrated ammonia to a saturated solution of the acid in acetone till slightly alkaline, when the ammonium salt was obtained as a bluish-grey glistening crystalline precipitate which after drying was recrystallised from water.

Other salts were prepared by adding a solution of a salt of the metal whose salt was to be prepared to a solution of the ammonium salt in water when the metallic derivative was thrown down as a precipitate This was washed with hot water, crystallised from acetone and the percentages of metal and sulphur were estimated by the usual methods

The silver salt is photo-sensitive and decomposed very slowly on keeping. Other salts are quite stable and melt above 200° C with decomposition. All the salts of diphenyl-thiovioluric acid possess beautiful crystalline structure and are highly soluble in acetone and less so in alcohol or ether The absorption maxima of a number of them were also found out.

Summary and Conclusions

1. The metallic salts of *iso*-nitroso-diphenyl-thiobarbituric acid have been prepared for the first time with a view to study their colour in relation to chemical constituents.

2. The change of colour from yellow to blue or green has been shown from theoretical considerations to be due to a fundamental change in the constitution of the molecule from an oximino-ketonic to a nitroso-enolic structure.

3. The change in structure produces a true nitroso group which from the point of view of the theory of colour on the basis of molecular strain,

has been shown to be a highly strained group which thus gives intense colour to the salts.

4. From theoretical considerations, the salts appear to be internally complex compounds and structural formulæ have been given on this basis.

The authors wish to express their indebtedness and sincere thanks to Prof S. Dutt for his kind interest in the work.

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1-NITRO-2-HYDROXY-3-NAPHTHOIC ACID AND ITS DERIVATIVES

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6-Nitro-2-hydroxy-3-naphthoic acid is obtained by the nitration of 1-amino-2-hydroxy-3-naphthoic acid or its diazo-oxide and subsequent elimination of the amino or diazo group (*I. G. Farbenind.* A. G., Ger 623496; General Aniline Works, U.S. 2040587; *I. G. Farbenind.* A. G., Brit. 445278). This 1-amino-2-hydroxy-3-naphthoic acid has been prepared by various indirect methods (Mohlau, *Ber*, 1893, **26**, 3066; Mohlau and Kriebel, *Ber*, 1895, **28**, 3091; Weil and Heerdt, *Ber.*, 1922, **55**, 226). Robertson (*J pr. ch*, 1893, (2), **48**, 534), however, claims to have obtained it by the reduction of 1-nitro-2-hydroxy-3-naphthoic acid which in its turn is obtained by the nitration of 2-hydroxy-3-naphthoic acid, but no experimental details are available and the melting point of the nitro acid given by this author is 233–38° which is quite different from the one described here (246–48°) and therefore his nitro acid may not be pure.

Later Gradenwitz (*Ber.*, 1894, **27**, 2623) nitrated methyl 2-hydroxy-3-naphthoic acid and got simple phthalic acid by the oxidation of the nitro derivative obtained. He thus proved isonuclear positions of –OH, –COOH and $-NO_2$ groups, but he did not definitely name the susbtance. But the only possible position taken up by the nitro group, according to the directing influences of –OH and –COOH groups, is 1 only. His nitro derivative must, therefore, be methyl 1-nitro-2-hydroxy-3-naphthoate.

In the present work the methyl and ethyl esters of 2-hydroxy-3-naphthoic acid are nitrated according to Gradenwitz (*loc. cit*) and free acid is obtained by hydrolysis with alcoholic potassium hydroxide. 1-Nitro-2-hydroxy-3-naphthoic acid melts at 246–48°.

The ethyl ester of the nitro acid has the melting point 155–56°, identical with that described by Meisenheimer, Theilcker and Beißwenger (*Ann.*, 1932, **495**, 275) who have not given experimental details.

The acid chloride of 1-nitro-2-hydroxy-3-naphthoic acid is easily obtained. From this acid chloride, some derivatives like ethyl esters and arylamides are prepared from aniline, *o*-, *m*-, and *p*-toluidines and *o*-, *p*-, anisidines.

Experimental

1-Nitro-2-hydroxy-3-naphthoic acid.—A mixture of methyl 1-nitro-2-hydroxy-3-naphthoate (or the ethyl ester) (10 g), rectified spirit (50 c.c) and potassium hydroxide (100 c c of 2 N) was refluxed on boiling water-bath for about two hours. The acid, that separated on acidification, was crystallised from dilute alcohol in shining yellow needles, m.p. 246–48°. (Found: N, 6 0%; $C_{11}H_7O_5N$ requires N, 6 0%.)

1-Nitro-2-hydroxy-3-naphthoyl chloride—A mixture of 1-nitro-2-hydroxy-3-naphthoic acid (1 g), phosphorous pentachloride (2 g) and dry chloroform (25 c c) was refluxed on boiling water-bath until a clear solution was obtained. On cooling the reaction mixture, the acid chloride separated in brownish yellow needles, which were filtered and washed with dry petroleum ether and dried under vacuum over phosphorous pentoxide, m p. 168–70°. (Found: Cl, 14·2%. $C_{11}H_6O_4NCl$ requires Cl, 14·1%)

Phenyl-1-nitro-2-hydroxy-3-naphthoate.—It is prepared by heating together a mixture of acid (2 g), phosphorous oxychloride (1 c c) and phenol (2 g.) at 140-50° until effervescence ceases The mixture is cooled, diluted with water and washed.

Table I

Derivatives of 1-*nitro-2-hydroxy-3-naphthoic acid*

	Name	Formula	Appearance	Melting point	Nitrogen	
					Found	Required
1	Phenyl-1 nitro 2-hydroxy-3-naphthoate	$C_{17}H_{11}O_5N$	Thick flat needles	170–71°	4·7%	4·5%
2	Ethyl 1 nitro 2 hydroxy 3 naphthoate	$C_{13}H_{11}O_5N$	Yellow needles	155–56°	5·1%	5·4%
3	1-Nitro-2-hydroxy-3-naphthanilide	$C_{17}H_{12}O_4N_2$	Small yellow needles	188–89°	9·5%	9·1%
4	1-Nitro-2-hydroxy-3 naphtho-toulidide	$C_{18}H_{14}O_4N_2$	Orange needles	190–91°	9·2%	8·7%
5	1 Nitro-2-hydroxy-3 naphth *m*-toulidide	$C_{18}H_{14}O_4N_2$	Pale yellow needles	196–97°	9·0%	8·7%
6	1 Nitro-2-hydroxy-3-naphtho-toulidide	$C_{18}H_{14}O_4N_2$	Long pale yellow needles	199–200°	9·3%	8·7%
7	1-Nitro-2-hydroxy 3 naphtho-anisidide	$C_{18}H_{14}O_5N_2$	Yellow flat needles	224–25°	8·4%	8·3%
8	1-Nitro-2-hydroxy-3-naphtho-anisidide	$C_{18}H_{14}O_5N_2$	Yellow needles	210–11°	8·9%	8·3%

The arylamides are prepared by leaving the mixture of the amine and acid chloride in presence of dry benzene for an hour and washing the solid obtained with dilute hydrochloric acid after the removal of the solvent. They are crystallised from glacial acetic acid. They are described in Table I.

SUMMARY

Free 1-nitro-2-hydroxy-3-naphthoic acid is isolated, its acid chloride, phenyl ester and anilide, *o*-, *m*-, *p*-toulidides and *o*- and *p*-anisidides are prepared.

THE ACTION OF HEXAMETHYLENETETRAMINE ON THE METHYL ESTERS OF PHENOL-CARBOXYLIC ACIDS

Part V. The Derivatives of 2: 4-Dihydroxy-5-Formylbenzoic Acid

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THE preparation as well as the characterisation of 2 4-dihydroxy-5-formylbenzoic acid has already been described by Desai and Radha.[1] Some of its important and interesting derivatives are being described in this communication. Attempts to esterify the carboxyl group by Fischer-Speier method resulted in the formation of some colouring matter. The action of either diazomethane, or dimethylsulphate in an alkaline medium or the action of methyl iodide on the silver salt of the acid resulted in the methylation of only one of the hydroxyl groups, and various other methods of methylation failed to give the dimethoxy derivative. The monomethoxy derivative may be either 2-methoxy-4-hydroxy-5-formylbenzoic or 2-hydroxy-4-methoxy-5-formylbenzoic acid.

Nitration of 2:4-dihydroxy-5-formylbenzoic acid gave a mixture of 2.4-dihydroxy-5-nitrobenzaldehyde and 2·4-dihydroxy-3 : 5-dinitrobenzoic acid, and it was not possible to isolate the nitro-derivative containing both the formyl and carboxyl groups in tact.

Clemmenson reduction gave readily 2 : 4-dihydroxy-5-methyl-benzoic acid, while bromination of the aldehyde acid under various conditions gave a bromo-derivative which gave too low values for the halogen. Acetylation of the aldehydo acid with acetic anhydride in presence of either pyridine or anhydrous sodium acetate gave only the di-acetoxy derivative, not a trace of the coumarin which was expected in the latter method being formed.

Condensation of the aldehydo acid with ethyl malonate and ethyl acetoacetate by Knoevenagel's method gave respectively 3-carbethoxy-6-carboxy-7-hydroxy coumarin and 3-acetyl-6-carboxy-7-hydroxy coumarin, the alkaline solutions of which gave blue fluorescence. The formation of these two coumarin derivatives furnish the additional proof to establish the 5-position of the formyl group.

Experimental

Methylation of 2 4-dihydroxy-5-formylbenzoic acid and formation of 2 or 4-methoxy-4 or 2-hydroxy-5-formylbenzoic acid.—To the aldehydo-acid (1 gm.) dissolved in potassium hydroxide (100 c c of 20%), dimethylsulphate (20 c c) was gradually added with shaking and warmed on the water-bath for one hour. The yellow, flocculent precipitate obtained on the acidification with hydrochloric acid crystallised from methyl alcohol in small yellowish needles, m.p 246–47 It gave an intense red coloration with alcoholic ferric chloride (Found: C, 54·8; H, 3 9, $C_9H_8H_8$ requires C, 55 1; H, 4·0 per cent)

Nitration of 2·4-dihydroxy-5-formylbenzoic acid and formation of 2·4-dihydroxy-5-nitrobenzaldehyde and 2 4-dihydroxy-3 5-dinitro-benzoic acid.—

Concentrated nitric acid (15 c c.) was gradually added with constant stirring to the solution of the aldehydoacid (2 g) dissolved in concentrated sulphuric acid (10 c c.), and left in a frigidaire overnight The solid that separated out was filtered, washed and crystallised from dilute alcohol in long, lustrous, golden-yellow needles, m p 146–47° It did not dissolve in sodium bicarbonate solution, but readily reacted with 2.4-dinitrophenylhydrazine and identified as 2·4-dihydroxy-5-nitrobenzaldehyde of Gattermann.[8] (Found: N, 7 4; $C_7H_5O_5N$ requires N, 7·7 per cent)

The 2: 4-dinitrophenylhydrazone prepared in the usual manner crystallised from glacial acetic acid in small, orange needles, m.p. 258° (dec) (Found: N, 19 5; $C_{13}H_9O_8N_5$ requires N, 19 3 per cent.)

The filtrate from which the nitro-aldehyde was removed was diluted with water, salted, and extracted with ether. On the removal of the solvent small yellow crystals of a solid, m p 195–96°, were obtained It dissolved in sodium bicarbonate solution with effervescence, but did not react with 2.4-dinitrophenylhydrazone, and was identified as 2.4-dihydroxy-3.5-dinitrobenzoic acid by comparison with an authentic specimen prepared by Hemmel Meyer's[3] method (Found N, 11 2; $C_7H_4O_8N_2$ requires N, 11·5 per cent.)

2.4-Dihydroxy-5-methylbenzoic acid was prepared by adding the alcoholic solution of the aldehydo acid (2 g) to amalgamated zinc (40 g.) and dilute hydrochloric acid (50 c.c.) and warming the mixture on the water-bath for 2 hours The hot liquid deposited small needles, m.p 163–64° C (Found: C, 58·2; H, 4 5; $C_8H_8O_4$ requires C, 58·3; H 4 8 per cent)

2: 4-Diacetoxy-5-formylbenzoic acid was obtained by heating the mixture of the formyl acid (1 g.), acetic anhydride (10 c.c) and pyridine (3 drops)

on a sand-bath for four hours. The pasty mass obtained on pouring the mixture into water crystallised from dilute alcohol in long, colourless needles, m p. 158–59° C. and did not give any colouration with alcoholic ferric chloride. (Found. C, 53·8, H, 3 8; $C_{12}H_{10}O_7$ requires C, 54·1, H, 3·8 per cent.)

Ethyl 7-hydroxy-6-carboxy-coumarin-3-carboxylate.—A mixture of the aldehydo acid (2 g.), ethyl malonate (2 g.), pyridine (20 c.c.) and piperidine (4–5 drops) was kept overnight after heating on the water-bath for one hour. The pasty solid obtained on the addition of dilute hydrochloric acid crystallised from alcohol in pale-yellow needles, m p 235–36° C. (Found: C, 57 0; H, 4 2, $C_{14}H_{10}O_7$ requires C, 56 7, H, 3 9 per cent.)

7-Hydroxy-6-carboxy-3-acetylcoumarin was obtained by heating the mixture of the formyl acid (1 gm.), ethylacetoacetate (1 g), pyridine (10 c.c.) and piperidine (4 drops) on the water-bath for one hour and keeping the mixture overnight. The solid obtained on acidification with dilute hydrochloric acid crystallised from dilute alcohol in needles, m p. 167–68° C. The alcoholic solution of this substance as well as the one described above gave a reddish-brown colouration with alcoholic ferric chloride. (Found: C, 58·2; H, 4·0; $C_{12}H_8O_6$ requires C, 58 1; H, 3 8 per cent.)

Summary

Some important and interesting derivatives of 2:4-dihydroxy-5-formylbenzoic acid have been prepared

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STUDIES IN NAPHTHALENE SERIES

Part X. The Preparation and the Properties of 1-Stearyl-, 1-Palmityl- and 1-Lauryl-2-Naphthols

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IN continuation of our work in this series, we have studied the preparation and the properties of 1-stearyl,-1-palmityl-, and 1-lauryl-2-napthols, and many interesting results have been obtained 1-stearyl-2-napthol (I, R $= C_{17}H_{35}$) was readily obtained by the application of the Nencki Reaction to β-naphthol and stearic acid This hydroxy-ketone which did not give any colouration with alcoholic ferric chloride was characterised by its *p*-nitrophenylhydrazone, and was methylated to 2-methoxy-1-stearyl-naphthalene The Clemmenson reduction gave exclusively 1-octadecyl-2-naphthol, unaccompanied by any neutral hydroxylic product

The Kostanecki acylation with acetic anhydride and sodium acetate gave 2-methyl-3-hexadecyl-1 : 4-β-napthapyrone (II), the alkaline hydrolysis of which gave the original ketone (I) The condensation of the ketone (I) with ethylbromacetate gave ethyl 1-stearyl-β-naphthoxyacetate (III, R = $C_{17}H_{35}$), which on treatment with sodium ethoxide in absolute alcoholic solution gave 2-carbethoxy-3-hepadecyl-β-naphthacoumarone (IV, R $C_{17}H_{35}$), the corresponding acid of which on decarboxylation yielded 3-heptadecyl-β-naphthacoumarone (V, R $= C_{17}H_{3}$)

The preparation and properties of 1-palmityl-and 1-lauryl-2-naphthols being similar to those of 1-stearyl-2-naphthol have been fully described in the experimental portion.

EXPERIMENTAL

1-Stearyl-2-naphthol.—An intimate mixture of stearic acid (19 g.), β-naphthol (7 g.) and powdered anhydrous zinc chloride (7 g.) was heated in an oil-bath at 180° C. for three hours. The warm product was poured into water containing some dilute hydrochloric acid, and the precipitated solid was filtered off and washed with water. It was then treated with 5% sodium bicarbonate solution to remove the unreacted stearic acid. The pure product crystallised from alcohol in white lustrous, small needles, m.p.

125-126° C (depressed to 90-91° by β-naphthol). Its alcoholic solution did not give any colouration with ferric chloride It was insoluble in dilute caustic soda solution, but soluble in most of the organic solvents (yield = 30 p.c) (Found: C, 81 7, H, 10·1, $C_{28}H_{42}O_2$ requires C, 81 9; H, 10 2 per cent)

The p-*nitrophenylhydrazone* was prepared by heating the ketone (0 5 g.) and 4-nitrophenylhydrazine (0·5 gm) in alcohol (20 c c) under reflux for six hours. The hydrazone crystallised in reddish lustrous plates m.p 260–61° C (Found. N, 7 5; $C_{34}H_{47}N_3O_3$ requires N, 7 7 per cent)

1-*Stearyl*-2-*methoxy-naphthalene* —A mixture of 1-stearyl-2-naphthol (1 g.) anhydrous potassium carbonate (2 g.) dimethyl sulphate (5 c.c) and dry acetone (20 c.c.) was refluxed on water-bath for 6 hours. The solution was filtered and after the removal of acetone the methylated product crystallised from petroleum ether in white, lustrous needles, m.p 72·73° C (Found· C, 82·2; H, 10·2; $C_{29}H_{44}O_2$ requires C, 82·1; H, 10·4 per cent)

Clemmenson reduction of 1-*stearyl*-2-*naphthol-preparation of* 1-*Octadecyl* 2-*naphthol* —A mixture of dilute hydrochloric acid (1 : 1; 35 c.c.), amalgamated zinc (5 g.), and 1-stearyl-2-naphthol (1 g) dissolved in alcohol (20 c c), was heated on sand-bath under reflux for 6 hours The cold mixture was diluted with water and extracted with ether. The ethereal layer was extracted with alkali, and the alkaline solution when acidified gave a white product which crystallised from alcohol in white plates, m p. 75–76° C. (Found: C, 84·5, H, 11 3; $C_{28}H_{44}O$ requires C, 84·4, H, 11·1 per cent.)

Kostanecki reaction with 1-*stearyl*-2-*naphthol and formation of* 2-*methyl*-3-*hexodecyl*-1 : 4-β-*naphthapyrone* —A mixture of 1-stearyl-2-naphthol (1 g), powdered anhydrous sodiumacetate (1 g) and acetic anhydride (10 c c) was heated in an oil-bath at 175–180° C for 14 hours and then poured in water. The white product which separated out was crystallised from alcohol in white, lustrous, small needle, m.p 79–80° C It was soluble in usual organic solvents and dissolved in concentrated sulphuric acid giving a reddish brown colour. (Found: C, 82·8; H, 9 6, $C_{30}H_{42}O_2$ requires C, 82 9; H, 9·7 per cent)

Hydrolysis of the pyrone to stearyl-2-*naphthol* —The pyrone was boiled with 10 per cent. alkali under reflex for three hours. On acidifying the alkaline solution, a white product was obtained, which crystallised from alcohol in white needles, m.p. 125–126° C. and was identified as stearyl-2-naphthol by mixed m.p.

Condensation of 1-stearyl-2-naphthol with ethyl bromacetate and the preparation of ethyl-1-stearyl-p-naphthoxyacetate. A mixture of 1-stearyl-2-naphthol (4 g.), potassium carbonate (1 g), ethyl bromacetate (4 c c.) and dry acetone (35 c.c.) was heated on water-bath under reflux for five hours On removing acetone, a yellowish brown liquid was obtained which was washed with water, extracted with ether, dried and recovered It was a pale-yellow, oily liquid b p 279° C (Found. C, 77 4, H. 9 8, $C_{32}H_{48}O_4$ requires C, 77 3; H, 9 7 per cent)

Hydrolysis of ethyl-1-stearyl-β-naphthoxy acetic acid and the preparation of 1-stearyl-β-naphthoxy acetic acid —The above ester (1 g.) was boiled with 10% alcoholic alkali (20 c.c) under reflux for three hours. On removing alcohol and acidifying the alkali solution, a white product was obtained which was crystallised from alcohol in white flakes, m p. 66–67° C (Found: C, 76·8, H, 9 6; $C_{30}H_{44}O_4$ requires C, 76·9, H, 9·5 per cent.)

The p-nitrophenyl-hydrazone of the acid prepared by the usual manner crystallised from alcohol in deep-red shining plates m p. 220–221° C (Found: N, 6 9; $C_{36}H_{49}O_5N_3$ requires N, 7 0 per cent)

Action of sodium ethoxide on ethyl-1-stearyl-β-naphthoxy acetate and the preparation of 2-carbethoxy-3-heptadecyl-β-naptha coumarone.—The β-naphthoxy acetate (5 c.c.) was mixed with sodium ethoxide in absolute alcohol (Na = 2 gm.; alcohol = 40 c c) and the solution was heated on water-bath under reflux for three hours. On evaporating the alcohol, a colourless liquid was obtained B P. 265° C (Found: C, 80·5, H, 9·8; $C_{33}H_{46}O_3$ requires C, 80 3; H, 9·7 per cent.)

Hydrolysis of the above naphthacoumarone to 2-carboxy-3-heptadecyl-β-naphtha coumarone —The above ester (3 g.) was boiled with 10 per cent. alcoholic alkali (30 c c) for three hours. The solid obtained on the removal of alcohol and acidification from hexane in white, flat needles m.p 60–61° C (Found: C, 79 8; H, 9 5, $C_{30}H_{42}O_3$ requires C, 79·9; H, 9 3 per cent.)

Decarboxylation of 2-carboxyl-3-heptadecyl-β-naphtha coumarone to 3-heptadecyl-β-naphtha coumarone —The above acid was introduced in a flask and heated at 80° C for four hours The brown product obtained after washing the residue with dilute alkali crystallised from hexane in white, small needles, m.p 49–50° C (Found C, 85·5, H, 10 5, $C_{29}H_{48}O$ requires C, 85 7; H, 10·4 per cent.)

1-Palmityl-2-naphthol prepared from β-naphthol (7 g), palmitic acid (16 g.) and zinc chloride (7 g.) crystallised from alcohol in white, small plates, m p. 115–16° C. (depressed to 85–86° C by β-naphthol). Its

alcoholic solution gave no colouration with ferric chloride (yield 28 per cent.). (Found: C, 81 8; H, 9 7; $C_{36}H_{60}O_2$ requires C, 81 7; H, 9·9 per cent.)

The p-*nitrophenylhydrazone* of the ketone was crystallised from alcohol in red flakes, m.p. 195–96° C. (Found· N, 8·1, $C_{42}H_{63}O_2N_3$ requires N, 8·1 per cent.)

1-*Palmityl*-2-*methoxy-naphthalene* crystallised from petroleum ether in white lustrous soft needles, m.p. 68–69° C. (Found: C, 81 9; H, 10·3; $C_{27}H_{46}O_2$ requires C, 81 8, H, 10 1 per cent.)

1-*Hexadecyl*-2-*naphthol* prepared by the clemmenson reduction was crystallised from alcohol in white small plates m p 70–71° C (Found: C, 84 2; H, 10·8; $C_{36}H_{40}O$ requires C, 84 4; H, 10 9 per cent.)

2-*Methyl*-3-*tetradecyl*-1 . 4-*β-naphthapyrone* was crystallised from alcohol in small, white, lustrous needles, m p. 73–74° C. It was soluble in usual organic solvents and its solution in concentrated sulphuric acid gave brownish-yellow colouration. (Found. C, 82·9, H, 9 2, $C_{38}H_{50}O_2$ requires C, 82 8, H, 9 4 per cent.) The chromone on hydrolysis with dilute alkali gave the original ketone.

Ethyl-1-*palmityl-β-naphthoxy acetate* was obtained from the ketone and ethyl brom-acetate as a yellow, oily liquid, b.p 263° C. (Found· C, 76·8; H, 9·7; $C_{30}H_{44}O_4$ requires C, 76·9; H, 9 5 per cent.)

1-*Palmityl-β-naphthoxy-acetic acid* prepared by the hydrolysis of ethyl-1-palmityl-β-naphthoxy acetate by alkali was crystallised from alcohol in white lustrous plates, m.p. 64–65° C (Found. C, 76·5, H, 9 1, $C_{28}H_{46}O_4$ requires C, 76 3; H, 9·2 per cent)

The p-*nitrophenylhydrazone* of the 1-palmityl-β-naphthoxy acetic acid was obtained from alcohol in red, lustrous, small flakes, m.p. 210–11° C (Found. N, 7·1; $C_{34}H_{48}O_5N_2$ requires N, 7 3 per cent.)

2-*carbethoxy*-3-*pentadecyl-β-naphtha coumarone* prepared from ethyl-1-palmityl-β-naphthoxy acetate and sodium ethoxide was a colourless oily liquid b p. 245° C (Found: C, 80 2; H, 9 3, $C_{30}H_{42}O_3$ requires C, 80 0; H, 9·4 per cent)

2-*Carboxy*-3-*pentadecyl-β-naphtha coumarone* obtained by the hydrolysis of 2-carbethoxy-3-pentadecyl-β-naphtha coumarone, was crystallised from petroleum ether in white plates, m.p. 56–57° C. (Found: C, 79·7, H, 9·3; $C_{28}H_{38}O_3$ requires C, 79 6; H, 9 1 per cent.)

3-*Pentadecyl-β-naphtha-coumarone* prepared by decarboxylating the above was crystallised from petroleum ether in white lustrous, small plates,

m.p. 45 46° C. (Found: C, 85·8; H, 10 3, $C_{27}H_{32}O$ requires C, 85 7; H, 10·1 per cent.)

1-*Lauryl*-2-*naphthol* prepared from β-naphthol (7 g) lauric acid (14 g.) and zinc chloride (7 g.) crystallised from alcohol in white, lustrous flakes, m.p. 95–96° C It was soluble in usual organic solvents (yield 25 per cent.) (Found: C, 80 7, H, 9·3 $C_{22}H_{30}O_2$ requires C, 80 9; H, 9·2 per cent.)

The p-*nitrophenylhydrazone* of the ketone crystallised from alcohol in yellowish-red, small needles m p. 165–66° C (Found: N, 9 0; $C_{28}H_{35}O_2N_3$ requires N, 9 1 per cent.)

1-*Lauryl*-2-*methoxy-naphthalene* crystallised from petroleum ether in white, flat needles, m.p. 54 55° C. (Found: C, 81·3; H, 9 6; $C_{23}H_{32}O_2$ requires C, 81 2; H, 9·4 per cent)

1-*Dodecyl*-2-*naphthol* crystallised from alcohol in white lustrous, small plates, m.p. 65–66° C (Found: C, 84 4; H, 10 2; $C_{22}H_{32}O$ requires C, 84·5; H, 10 3 per cent)

2-*Methyl*-3-*decyl*-1 : 4-β-*naphthapyrone* crystallised from alcohol in white shining small flakes, m p. 69–70°C Its solution in concentrated sulphuric acid gave brownish-yellow colouration. (Found· C, 82·4; H, 8·5; $C_{24}H_{30}O_2$ requires C, 82·2; H, 8·6 per cent.) The pyrone on alkaline hydrolysis gave the original ketone

Ethyl-1-*lauryl*-β-*naphthoxy-acetate* was obtained as a straw-yellow, oily liquid, b p. 230° C., from ethyl brom-acetate and 1-lauryl-2-naphthol. (Found· C, 75·9; H, 8 7; $C_{30}H_{44}O_4$ requires C, 75 7; H, 8·8 per cent.)

1-*Lauryl*-β-*naphthoxy-acetic acid* crystallised from alcohol in white, shining plates, m.p. 47–48° C (Found· C, 74·8; H, 8 6; $C_{24}H_{32}O_4$ requires C, 74 9; H, 8 4 per cent)

The p-*nitrophenyl hydrazone* of the above naphthoxy acid crystallised from alcohol in red plates, m.p. 200–01° C. (Found: N, 8·3; $C_{30}H_{37}O_5N_3$ requires N, 8·1 per cent)

2-*Carbethoxy*-3-*undecyl*-β-*naphtha coumarone* was obtained as a colourless oily liquid, b.p. 215° C., by the action of sodium ethoxide on ethyl-1-lauryl-β-naphthoxy acetate. (Found C, 79·2; H, 3 5, $C_{30}H_{34}O_3$ requires C, 79 1; H, 8 7 per cent)

2-*Carboxy*-3-*undecyl*-β-*naphtha-coumarone* crystallised from petroleum ether in white small plates, m.p. 42–43° C (Found: C, 78·8; H, 8·3; requires C, 78·7; H, 8·2 per cent)

3-*Undecyl-β-naphtha coumarone* was crystallised from hexane in white, lustrous plates, m p. 36–37° C (Found C, 85 6; H, 9 5; $C_{29}H_{38}O$ requires C, 85·7, H, 9 4 per cent)

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SUMMARY

1-Stearyl, 1-palmityl, and 1-lauryl-2-naphthols have been prepared by the Nencki process These hydroxy ketones were methylated, and reduced by Clemmensen's method They were subjected to the Kostanecki reaction, and condensed with ethyl bromacetate, to obtain the chromones and coumarones containing these long-chain alkyl groups

A CHEMICAL AND PETROLOGICAL STUDY OF SOME DYKE ROCKS IN THE PRE-CAMBRIAN (CUDDAPAH TRAPS)*

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Introduction

The suite of traps that forms the subject of this paper occurs as intrusions in the Vempalle limestones and the Tadpatri shales of the Lower Cuddapahs in the Pulivendla taluk of Cuddapah, the Tadpatri taluk of Anantapur and the Dhone taluk of Kurnool They were collected from a large area in the Cuddapah basin extending from Betamcherla in the Kurnool district to near Vempalle in the Cuddapah district, so that they are representative of the numerous sills that traverse the area. The collection includes also two or three specimens of trap rocks intrusive into the Archaean gneisses near Tiruttani in the Chittoor district Judging from petrological characters the Tiruttani rocks are probably of the same age as that of the Cuddapah traps, but we have no stratigraphical data to determine the relationship between these two.

These traps form numerous sills and are occasionally lenticular though generally regular and of uniform thickness The thicker sills often contain intercalations of Vempalle limestones or Tadpatri shales. They are fine-grained and of uniform grain, being composed generally of labradorite feldspar, augite and micropegmatite with subordinate biotite, magnetite, epidote, glass and secondary alteration products. It is only rarely that they exhibit any difference in the grain-size between the centre and the margins. Such a sill, composite in nature, is seen passing through Pulivendla as noted by Dr. C. S. Fox. The central portion of the sill is very basic and contains coarse grains of abundant olivine, augite, enstatite, serpentine, a little feldspar, iron ore and brown mica and thus differs from the layers above and below it, which are dolerites without olivine. The trap sills are fairly conspicuous because of their forming dark low ridges which are marked by brown coloured soil and thorny shrubs. In some places the rocks show the presence of amygdaloidal cavities filled up with secondary infillings and

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are also traversed by veins of epidote which shows up well because of its marked green colour.

The Cuddapah traps have not been studied by any one so far in any detail As early as 1890, P. Lake described briefly the olivine-bearing traps of Juturu Subsequently (Sir) T H Holland (1897 B) classified "some dykes of basic igneous rocks which break through the 'pyroxene granulites' and which he regarded as the dyke-representative of the Cuddapah lava flows" and gave a mineralogical description of these rocks More recently (Sir) C. S. Fox (quoted by A. L. Coulson, 1934) and A L Coulson (1933, 1934) have referred to these traps only incidentally in their description of asbestos and barytes occurrences in the Cuddapah formations. No chemical data are available except for the two modern analyses given by A. L. Coulson in his memoir on asbestos (1934) and the two much earlier analyses given by Holland in 1897

In the following pages are described the petrographic and chemical characters of these trap rocks. The chemical analyses were done in the Geology Department of the Presidency College, Madras The analytical results are subjected to the petrochemical studies introduced by Prof. Dr. P. Niggli of Zürich. The plagioclase feldspars and pyroxenes have been studied by the Universal Stage methods, which include the twinning laws and other optical characters The textural relationship exhibited by the rocks has also been studied in detail, which showed that these minerals have crystallised simultaneously to a large extent

It has been possible from these studies to trace the chemical characters of these traps, the trends of differentiation of the magma in the evolution of the various types, and the sequence of crystallisation of these traps in the differentiation history. The general results show that the magma which gave rise to the Cuddapah traps is of calc-alkali or tholeiite type. The Cuddapah traps are similar in many respects to the 'Newer dolerites' of Singhbhum, Keonjhar and other areas in the Iron ore series of Orissa and Singhbhum. They are also similar to the Gwalior traps in the nature of their pyroxenes, but are lower in alkalis and higher in alumina. They differ from the Deccan traps, the Karroo dolerites, the Tertiary dykes of the Island of Mull, the Whin Sill and the Palisades diabase in containing no pigeonite.

Mineralogy

Although uniform in their mineralogical characters and chemical composition the trap rocks under study may be divided into three textural groups,

1. *Fine-grained variety.*—This varies from dolerite to basalt and is usually dark in colour, compact and also highly vesicular.

2. *Medium-grained variety.*—This type is mostly black to dark-grey in colour and is represented by quartz dolerite.

3 *Coarse-grained variety* —This type, formed by the slow cooling of the magma is found to occupy mostly the middle portions of the dykes or sills It includes olivine dolerites and quartz dolerites

The grain-size of the minerals composing the rock varies on the average from 0·2 mm. to 0 5 mm in the fine-grained varieties, and 0·5 mm to 1 mm. in the medium-grained rocks, to more than 1 mm. in the coarse-grained types. The petrological characters of the various specimens collected are fairly uniform, but some of the vesicular basalts differ from the normal types in containing much palagonite, often to the exclusion of pyroxene.

Microscopic characters —One striking feature observed under the microscope is the relationship between feldspar and pyroxene. Small laths of feldspar are enclosed either partly or wholly in elongate or stumpy prisms of augite or the augite may be developed in irregular form in the interstices of the penetrating plagioclase laths. Besides this marked doleritic and sub-ophitic development of plagioclase and augite, ophitic, inter-granular and intersertal textures are also noticed. In the olivine-bearing types, olivine is enclosed by large prismatic crystals of pyroxene. Micropegmatite and quartz occur occasionally in the interstices of the feldspars and augites. In the fine-grained types these are represented by a vague mesostasis of weakly refracting glass with grains of opaque magnetite and imperfectly developed microlites of feldspar. Generally the magnetite is distributed evenly throughout the rock. Biotite and hornblende occur as alteration products. Apatite and specks of pyrite are the usual accessories. The rocks have been subjected to secondary alteration such as palagonitisation, sericitisation, serpentinisation and kaolinisation.

The vesicular and amygdaloidal basalts have their vesicles filled up by palagonite and calcite and occasionally also by quartz instead.

In the following paragraphs the feldspars, pyroxenes, micropegmatite and other minor constituents are described.

Plagioclase —Plagioclase is the dominant constituent of all the normal rocks examined, except in the olivine-bearing type in which it is subordinate in amount to olivine and pyroxene. Megascopically the feldspars are bluish to dark-grey in colour. The crystals exhibit generally polysynthetic twinning,

but simple twinning is also met with and occasionally untwinned plagioclase laths are found in association with quartz pieces.

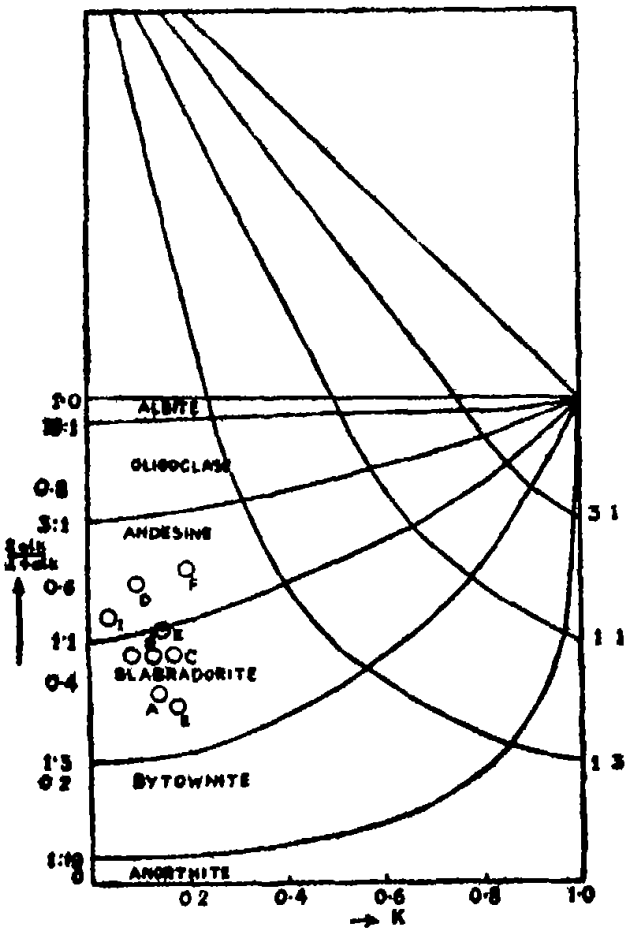


FIG. 1

$k - \frac{2\ alk}{al + alk}$ diagram for the Cuddapah Traps

The composition of the plagioclase feldspars and the twinning law obeyed by them were determined on the Federov Universal Stage. The anorthite content of the feldspars is found to vary from 75 to 30 per cent. Zoning is developed rather inconspicuously in most of the larger laths, being represented by a slight variation in the extinction angle towards the interior. In some cases, however, prominent zoning is observed, the composition passing from labradorite with about 60 per cent. anorthite to a thin external layer of andesine or oligoclase. The average composition of the plagioclase

is deduced to be near about 55 per cent anorthite and the first plagioclast to crystallise from the melt of this composition would contain about 75 per cent anorthite The feldspar phenocrysts found in the vesicular basalet (Type D, which is described later) do not show any marked zoning, the composition of these and of the groundmass feldspars being more or less the same It is porbable, therefore, that the early formed plagioclase has been 'made over' to the composition of the later feldspars with the result that zoning has disappeared The plagioclases exhibit predominantly twinning on (010) as the composition plane of different lamellæ with Albite and Carlsbad laws occurring frequently

The composition of plagioclase can also be deduced from the chemical analysis of the rock, if the calculated k and $\frac{2alk}{al+\bar{a}lk}$ values (Table V) are plotted in Niggli's diagram (Fig 1) It will be seen from the diagram that the nature of plagioclase deduced from the chemical composition of the rock agrees fairly well with optical determinations It may be pointed out that the average falls close to 55 per cent anorthite which is also the average arrived at from optical investigations. A and E have a higher anorthite content than the rest, but from the description of these rocks given elsewhere it will be seen that A is a highly basic rock belonging definitely to an earlier period in the history of consolidation, while E, if not so very basic, is highly feldspathic and also altered, which is reflected in the higher anorthite content of the rock.

Pyroxene.—The pyroxenes are found to belong mostly to the monoclinic variety. In the olivine-bearing types, however, rhombic pyroxenes were also noted in addition. The monoclinic pyroxene is usually augite with large optic axial angle; the other variety of monoclinic pyroxene, pigeonite with small optic axial angle was not detected in any of the analysed specimens but was present in slide No 8 (1 mile east of Vemula) in small amount

The monoclinic pyroxene is generally colourless in thin sections, but shows a slightly yellowish or greenish tinge, some grains are also pinkish, indicating that they are titaniferous. The mineral occurs in elongated or stumpy prisms generally twinned on (100) showing sometimes salite and herringbone structures It may also be irregular in shape, with two sets of cleavage. The optic axial angle varies from 40° to 56° and $Z \wedge C$ from 36° to 46°.

In the olivine-bearing types the rhombic pyroxene occurs in irregular form, intergrown with olivine and monoclinic pyroxene and is colourless.

The optic axial angle (negative) in the plane parallel to (010) varies from 79° to 85°. From this value a composition of En_{81} Fs_{19} is deduced from Burri's diagram (p. 181, 1941) for the rhombic pyroxene

Comparative study of the py oxenes found in this ancient intrusive rock with those in the basic rocks from India and from other parts of the world is interesting. Dr. L. A. N Iyer (1932) who investigated the 'Newer dolerites' of Bihar and Orissa found that the pyroxenes in them have a larger optic axial angle, varying from 56° to 68° but has not recorded any pyroxene of small optic axial angle Dr M S. Krishnan (1936) in his studies of the 'Newer dolerites' of Keonjhar State, Bihar and Orissa, did not report the presence of pigeonite in the dolerites and basalts, whereas in the norite dykes he was able to distinguish pyroxenes of small optic axial angle. In his paper on the Gwalior traps M. P Bajpai (1935) has not reported the optic axial angles of augites seen in the slides. P. R. J. Naidu* found that the 'abnormal' dolerite dykes cutting the charnockite areas of Halagur and Dodkanya, Mysore, contain pigeonite The pyroxenes of the Deccan traps have generally a small optic axial angle and belong to the pigeonite group as pointed by H. S. Washington (1922) and L. L. Fermor (1925) The Whin Sill (Holmes and Harwood, 1928), the Karroo dolerites (Daly and Barth, 1930, and Walker and Poldervaart, 1940) and the New Jersey diabases (Walker, 1940) exhibit characters similar to each other in having all the three pyroxenes—hypersthene, augite and pigeonite. In all these cases, there is a complementary relationship between hypersthene and pigeonite. In his latest paper on the 'Pyroxenes of common mafic magmas' H H. Hess (1941) has come to the interesting conclusion that the complementary relationship is due to the inversion of the lime-poor ortho-pyroxene to pigeonite at En_{70} Fs_{30}, so that for any ratio less than 7 : 3, pigeonite takes the place of the ortho-pyroxene.

This study shows that the Cuddapah traps contain predominantly monoclinic pyroxenes with large optic axial angle The dolerites of later ages appear to contain all the three pyroxenes, pigeonite being dominant in the normal Deccan traps. In view of the nature of the pyroxenes in these rocks, it would be pertinent to compare the normative composition and the metasilicate proportion of pyroxene, calculated from the average chemical composition with those of other rocks and see how this important difference can be accounted for (see Table I). The diopside and hypersthene molecules of the average Cuddapah traps and 'Newer dolerites' are similar except

* *Current Science*, 1943, 12, 115.

for a slightly higher content of these in the latter. The Karroo dolerites are also similar to the above dolerites in their containing more hypersthene than diopside. But, in contrast to this, the Deccan trap shows equal amounts of both these molecules The Whin Sill, though containing more hypersthene than diopside, shows less of both these molecules than the other rocks.

TABLE I

The normative composition of Pyroxenes in the Cuddapah traps and other dolerites and basalts

	Di	Hy	$CaSiO_3$	$MgSiO_3$	$FeSiO_3$
A	8 90	20 91	14 5	67 8	17·7
B	13·82	13 74	24·4	50·0	25 2
C	16 36	25·27	19 6	44 3	36·1
D	2 26	34 26	..	..	..
E	12 36	28·09	17 1	50	22 9
F	17 16	14 56	26·9	47·8	29·3
G	21·24	17 12	27 5	44·1	28·4
I	16 45	20 80	21·9	47 7	30 4
II	17·54	21·22	22·6	41·8	35 6
III	17·41	17·78	24·6	44 3	31 1
IV	16 76	25·74	19·6	46·6	33 8
V	13·14	15 90	22 3	52 3	25 4
VI	14·71	21·08	20·3	53 9	25 8

A to G Cuddapah traps.

I Average of 8 analyses of Cuddapah traps

II Newer dolerite. Average of 3 analyses of Newer dolerites, Singhbhum (L. A N. Iyer, 1932) and 2 of Keonjhar State (M. S Krishnan, 1936)

III Average of 11 analyses of Deccan traps (H S. Washington, 1922)

IV Average of 5 analyses of Karroo dolerites (Daly and Barth, 1930)

V Average of 6 analyses of Whin Sill (Holmes and Harwood, 1928)

VI. Average New Jersey basalt (Anderson, 1940)

The metasilicates in the averages of these rocks are remarkably uniform in showing a lower proportion of $CaSiO_3$ and higher proportion of $MgSiO_3$, while $FeSiO_3$ is intermediate between these values On a careful scrutiny it would appear that there is a reciprocal relationship between $MgSiO_3$ and $FeSiO_3$, for a decrease in $MgSiO_3$ results in the increase of $FeSiO_3$ but such a notable change is not observed in $CaSiO_3$ The explanation for this can be had from Fig. 2 which shows that pyroxenes of mafic magmas become enriched in iron and correspondingly impoverished in magnesium.

Thus, in view of the absence of any marked difference in the normative composition of the pyroxenes of the various rocks compared with the Cuddapah dolerites, the metasilicate proportions of the rocks analysed were plotted in the above figure. All except type A fall above the cotectic line.

This type is rich in olivine and carries rhombic pyroxene A study of the thin section goes to show that the rhombic pyroxene was the first to crystallise. The clino-pyroxene joined later and both crystallised out before the rhombic

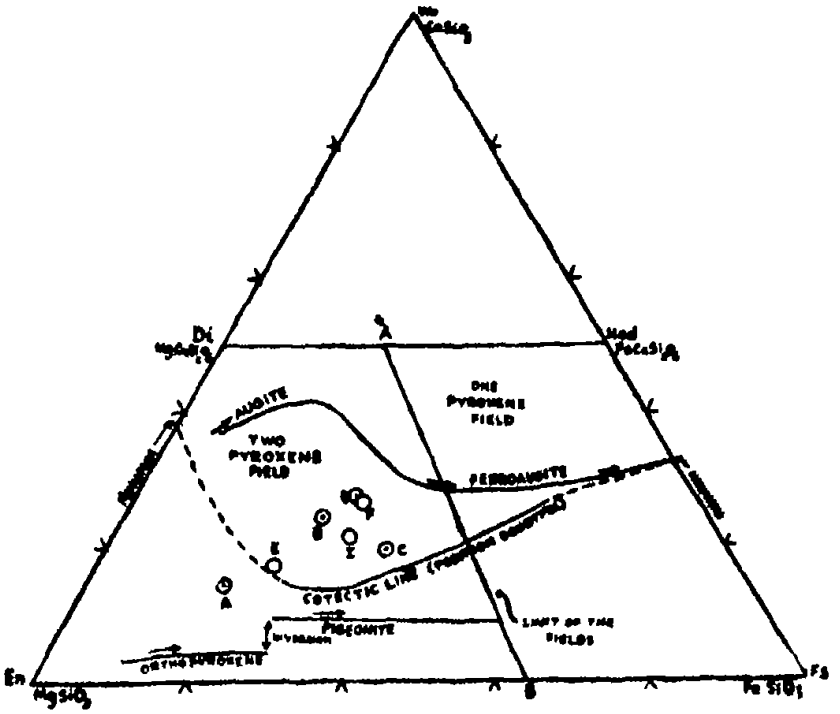


FIG 2

The trend of crystallisation of pyroxenes from mafic magmas (After H H Hess)

pyroxene reached the composition $En_{70}Fs_{30}$ In all the other rocks only one pyroxene was distinguished and the points for these rocks lie above the cotectic line. To account for the presence of only one pyroxene it could be reasonably supposed that the degree of reaction obtained between the melt and the crystals suspended in it was such that the melt never reached the cotectic line and this process might have been greatly assisted by the volatile constituents of the magma.

Pyroxene-Feldspar Relations and the Order of Crystallisation

To describe the different types of textural features in relation to the pyroxenes and feldspars various names have been proposed by different writers. Krokström (1933) has proposed four names, namely, ophitic, sub-ophitic, doleritic and sub-doleritic. The ophitic and sub-ophitic textures in basaltic rocks indicate that the feldspars are of earlier crystallisation while

the doleritic and sub-doleritic textures point to the simultaneous crystallisation of these minerals.

In the Cuddapah traps, the pyroxenes are generally larger in size than the plagioclases. The shapes of these pyroxenes are to a great extent determined by those of the adjacent feldspar laths Sometimes the pyroxenes are also sub-idiomorphic with a roughly prismatic habit Besides these, in some slides ophitic and sub-ophitic textures in the restricted sense of Krokström are also found, the pyroxenes then filling narrow interstices between two neighbouring feldspars, and different pieces over wide areas showing simultaneous extinction, with similar orientation or optical continuity The pyroxenes also enclose completely numerous small laths of plagioclase showing that they are definitely later than the plagioclase in crystallisation.

Barth (1936) has discussed the crystallisation process of basalt and suggested that the initial composition of the magma determines whether pyroxene or plagioclase is the first mineral to crystallise When crystallisation of the first mineral is going on, the melt moves towards the boundary surface where simultaneous crystallisation of both minerals would take place Barth has deduced, from a study of the plateau-basalts which show unequivocally simultaneous crystallisation of pyroxene and plagioclase, this boundary surface in a tetrahedron with the normative minerals *ab*, *an*, *di* and *hy* at the corners The position of the boundary surface is got from the sum of $ab' + 2\,di' + 2{\cdot}3\,hy'$, which is called the $f(norm)$. If the $f(norm)$ is near about 123 the basalt falls on or near about the boundary surface and simultaneous crystallisation is to be expected If the *norm* is smaller or greater than 123 the basalt lies in the plagioclase field or in the pyroxene field respectively. The $f(norm)$ values for the Cuddapah traps and for the other basalts compared with them are given in Table II

It will be seen from Table II that the $f(norm)$ is around 123 for all types except A, B and E which have a higher or lower value Type A is a rock of ultrabasic composition and from an examination of the thin section it is clearly seen that olivine and pyroxene are earlier than the plagioclase which is subordinate in amount and occupies the interstices between these minerals. In the rock designated B the pyroxenes are intergranular and intersertal to the feldspars which penetrate the former so that we can conclude that the feldspars crystallised earlier. The high percentage of alumina in this rock results in an excess of feldspar which causes crystallisation in the feldspar field itself. As has already been mentioned, the rock E shows high alumina percentage and the feldspars are extensively kaolinised so that the high per-

TABLE II

f (norm) for Cuddapah and other traps

	ab'	*an'*	*di'*	*hy'*	*f* (norm)
A	10·6	30 9	15·7	36 8	132·6
B	28·0	37·7	17·2	17·1	101·7
C	21·2	30·8	19 9	29·1	125·9
D	..	..	..	..	..
E	18·0	42 8	13·7	25·5	104·1
F	24·0	24·0	23·7	19·2	123·8
G	23 8	32 5	24 2	19·5	117 0
I	30·2	27·3	42·1	0·4	115·3
II	24 6	28·1	16 8	30·5	128·4
III	26 2	30·4	19·2	24 2	120·3
IV	27	29	22	22	122
V	29 3	25 6	20 4	24 7	126 9
VI	27·9	32·3	18 0	21 8	114·0
VII	20 5	32 5	20·5	26·5	122 5
VIII	29 2	28·3	17 4	25 1	121 7

A to II Cuddapah traps.
III Average of B to II
IV Average of 11 analyses of Deccan traps (Washington, 1922) As given by Barth (1936), Tab. 3, p 332
V. Newer dolerite Average of 3 from Singhbhum (L A N Iyer, 1932) and of 2 from Keonjhar State (M S. Krishnan, 1936)
VI Whin Sill Average of 6 analyses by Harwood (Holmes and Harwood, 1928).
VII. Karroo dolerite Average of 4 analyses (Daly and Barth, 1930) As given by Barth (1936), Tab 3, p 332.
VIII Average New Jersey basalt (Anderson, 1940)

centage of alumina may partly be due to alteration. But from the nature of the rock it can be said that even though some feldspars may have been precipitated first the bulk of them crystallised approximately simultaneously with the pyroxenes.

From these studies we can conclude that during the earlier stages of crystallisation—excepting in type A—the feldspars crystallised to begin with, but were very soon joined by the pyroxenes so that in all the normal types the two minerals have crystallised simultaneously.

Micropegmatite —There is some acid material in these basic dykes in the form of micropegmatite, quartz and acid glass, which are found in the interstices, forming a mesostasis to the earlier formed feldspars and pyroxenes; sometimes they may also form megascopic patches.

This acid material is considered by most petrologists as the last phase in the consolidation of the magma. It is present in many basic rocks in India and elsewhere. As early as 1897, Holland discussed the origin of

micropegmatite in the basic dykes of the Madras Presidency including those of Cuddapah age and concluded that the micropegmatite "is really original, the last phase in the consolidation of the rock" (p 34, 1897 A)

Bowen (pp 70-74, 1928) considers that quartz or acid residue in basic rocks is due to the early separation of olivine in excess of its stoichiometric proportion. But Fenner (1929 and 1931) objects to this theory on the ground that the earlier ferromagnesian silicates contain an excess of magnesia, while the residual liquid gets enriched in iron so that magnetite, pyroxene and feldspar crystallise during final stages. So he concludes that micropegmatite does not normally result from the process of crystallisation-differentiation, but is a secondary product of hydrothermal activity after the rock has completely solidified Kennedy (1933) advocates two distinct types of basaltic magmas, *viz.*, tholeiitic and olivine-basaltic types, and considers that the tholeiitic magma, represented by most plateau-basalts gives rise, on differentiation, to a liquid of acid composition and that the olivine-basalt (oceanic basalt) magma gives rise always to a liquid of feldspathoidal composition poor in quartz The Cuddapah trap would fall under the tholeiitic type as will also be pointed out later The tholeiitic type does not seem to have any significance in space and geological time as it is found in various ages in both fissure and central eruptions.

Minor Constituents

The other constituents seen in these rocks are biotite, amphibole, glass, chlorite, magnetite, hematite, epidote and clino-zoisite, apatite and pyrite with such secondary products as sericite, kaolin and calcite A short description of the more important of these is given below

Glass.—In all the fine-grained types the glass forms a mesostasis to the main constituents. It is colourless, light brown or dark in appearance and in almost all cases wholly devitrified, containing acicular crystals and microlites as also small rounded grains of magnetite.

Chlorite.—Both penninite and delessite are distinguishable. Penninite is greenish or bluish green in colour and weakly birefringent with 'ultra blue' interference colours. Delessite occurs in fibrous sheaves with positive elongation of the fibres, straight extinction and low birefringence It is pleochroic according to the general scheme:

$$Z = Y = \text{Green}, \quad X = \text{Straw yellow}$$

Iron ores.—Magnetite is found in all the rocks as an accessory mineral. It is in the form of large grains, sometimes with crystal contours and sometimes in granular clusters. The great part of this mineral is of an earl

generation, but in some cases evidence of late crystallisation is also found. The presence of leucoxenic material in some of the sections shows that part of it may be titaniferous.

Epidote and Clinozoisite —The epidote aggregates consist of minute grains recognised by their high refringence and birefringence They are strongly pleochronic, from very pale green to yellowish green. The clinozoisite is colourless to pale green and similar to epidote but shows very low birefringence It forms granular aggregates mostly derived from the alteration of feldspars

Petrographical Description and Chemical Analyses of the Cuddapah Traps

Seven representative specimens of traps from different localities in th area were chosen for chemical analyses so as to cover the general types encountered The analytical results and norms are given in Table III. The rocks are arranged in the order of increasing silica percentage but not necessarily in the order of increasing acidity as represented by saturation. The analysed types are briefly described below.

A *Picrite* (Hornblendeperidotitisch) —The rock is coarse-grained and dark in colour and is very largely made up of olivine and pyroxene. Olivine (0 2–0 9 mm) is colourless and mostly rounded in appearance with characteristic ' mesh ' structure having an optic axial angle (2V) of + 84° to + 88° Both ortho-pyroxene and clino-pyroxene are encountered. The ortho-pyroxene is enstatite occurring as large individuals (1 to 2·1 mm) of irregular shape The interference colours are 1st order grey to white and the optic axial angle (2V) in the plane perpendicular to *b*-axis is − 82° to − 84°. The clino-pyroxene (1 to 2 3 mm.) is intergrown with ortho-pyroxene and is mostly colourless, often with a yellowish tinge The optic axial angle is about + 50° to + 55° while the angle $Z \wedge C$ varies from 36° to 38°

The plagioclase which is subordinate in amount is largely altered and could not be determined, though showing broad lamellæ From Niggli's diagram and from the norm, the composition is deduced to be 62 per cent anorthite.

There are, in addition, alteration products, such as magnetite, serpentine, brown mica, sericite, kaolin and chlorite

The mode of the rock is given below:

Olivine	34·3	Chlorite and serpentine ..	17·9
Pyroxene (ortho & clino) ..	20·3	Biotite	4·4
Plagioclase	18·6	Magnetite	4·3

When the mode is compared with the norm, it will be seen that the amount of olivine actually present in the rock is less than the normative amount. The pyroxene and feldspar are also less than the normative percentages. But the modal magnetite is higher. Chlorite, serpentine and biotite make up this deficiency between the mode and the norm.

B *Pyroxene dolerite* (Normalgabbroid, c-gabbroid) —This rock is medium-grained and compact and bluish to dark-grey in colour and is made up of bluish plagioclase, dark dull pyroxenes and magnetite The plagioclase is seen in small slender laths (0 2 by 0 8 mm) developed in sub-ophitic relationship to pyroxenes. The feldspar is mostly labradorite with an anorthite content of 60 to 70 per cent.

The augite is always irregular in shape and faintly pinkish in colour with very weak pleochroism in yellowish or greenish tinges. The optic axial angle varies from $+41°$ to $+45°$ while the angle $Z \wedge C$ varies from 39° to 43°.

Chlorite, magnetite and sericite and kaolin occur as alteration products. Apatite is rarely found.

The mode of the rock is as follows:

Plagioclase	44 2	Magnetite	9 2
Pyroxene . ..	22·5	Sericite .. .	5·5
Chlorite . ..	18·8		

When the mode is compared with the norm it is seen that the amounts of feldspar and pyroxene are lower in the mode than in the norm. This we can expect from the alteration of the minerals

C. *Dolerite* (normalgabbroid; c-gabbroid).—The rock is dark-grey in colour, composed of greyish feldspars, dark ferromagnesians and a few pieces of magnetite. The plagioclase feldspars make up the bulk of the groundmass in the form of small laths (0·15 to 1 4 mm.) developed in sub-ophitic relationship to the pyroxenes which they penetrate from the edges and make the pyroxenes angular. A composition of about 55 per cent. anorthite is deduced from both Niggli's diagram and the norm They could not be determined on account of the alteration suffered by them.

The augite is colourless, occurring as large crystals twinned on (100) and encloses small laths of twinned plagioclase in addition to showing a marked doleritic structure. The optic axial angle (2V) in the plane parallel to (010) varies from $+44°$ to $+47°$ while $Z \wedge C$ in the same plane is 40° to 42·5°.

Micropegmatite and quartz pieces are also seen in the slide. As secondary minerals, magnetite, chlorite, kaolin, sericite and calcite are seen.

D. *Vesicular basalt-porphyry* (Natronlamprosyenitisch) —This is a dark-coloured rock with porphyritic crystals of feldspar embedded in a groundmass of chlorite and small feldspars of the same character. The rock is highly vesicular and the vesicles are filled up by dark, friable, chloritic material which has a dirty-green colour Inclusions of calcite and a dark-green or yellowish green mineral, not scratched by pen-knife, are seen in the chlorite.

The porphyritic plagioclases twinned according to Albite-Ala and Ala (Es) are found either as rectangular tables or as thick elongated prisms. The groundmass plagioclases are in the form of small laths and exhibit twinning after the same laws. The composition is 33 to 40 per cent. anorthite.

Clinozoisite and calcite are found associated with chlorite as they are the result of the alteration of feldspar. Clinozoisite, embedded in palagonite, is twinned on (100) showing the characteristic section of crystals of monoclinic symmetry. The extinction angle with reference to *c*-axis varies from 4° to 8°.

E *Quartz-dolerite* (Miharaitisch) —This is a medium-grained rock composed of greyish plagioclase and dark ferromagnesian minerals

Plagioclase is the most abundant mineral in the rock, giving lath-shaped sections. It is usually much altered to kaolin and sericite

The pyroxenes, often twinned on orthopinacoid, are irregularly shaped and sometimes prismatic and short. They are pale greyish yellow to colourless. The optic axial angle ($+2V$) in the plane parallel to (010) is from 52° to 56°. The angle between the axis of minimum elasticity and the vertical crystallographic axis is about 39°. Some of the pyroxenes are altered to serpentine.

Quartz and micropegmatite are intergrown with the feldspars. Some of the quartz may be of secondary origin on account of kaolinisation of feldspars. The minor constituents are magnetite, biotite and chlorite.

F *Fine-grained Basalt* (Melagabbrodioritisch).—This is a fine-grained cryptocrystalline dark-coloured rock composed of minerals indistinguishable even with the help of a good pocket lens The rock is merocrystalline under the microscope with imperfectly developed microlites of plagioclase embedded in a mosaic of pyroxene, palagonite and glass. Twinning is imperfectly developed. The composition is deduced as 39 per cent. anorthite from Niggli's diagram. The pyroxenes are seen as small rounded or rectangular,

pale yellow to colourless pieces with a tendency to be grouped in aggregates. Some rectangular prisms show simple twinning.

Magnetite occurs as relatively larger grains and enclose feldspars and pyroxenes. They are distinctly later than these minerals in consolidation. A few pieces of dichroic hæmatite are also seen.

The interstices of all these minerals are filled up by palagonite, ill-defined glass and chalcedony. A few pieces of zoisite and calcite are also noticed.

G. *Quartz-dolerite* (Miharaitisch).—This is a medium-grained dark-grey trap composed of grey plagioclase and dark ferromagnesian minerals. It shows two thin veinlets perpendicular to each other, consisting of palagonite which pass from one piece of chlorite or amphibole to another through feldspathic and micropegmatitic portions. It appears to have been formed as veins from magmatic fluids during the late stages of activity

The plagioclases occur as laths 3 to 7 mm. in length with ill-defined relationship to pyroxene. They show twinning after Albite, Carlsbad or Albite-Carlsbad law and contain between 54 and 70 per cent. of anorthite. Zoning as well as secondary alterations are observed.

The augite is colourless and non-pleochroic often exhibiting simple twinning on the orthopinacoid. The optic axial angle is $+ 49 \cdot 5^\circ$ and $Z \wedge C$ is 46°.

Micropegmatite generally fills the interspaces between pyroxenes and feldspars and is composed of quartz and feldspar, intergrown micrographically. The quartz carries inclusions of bluish crystals, probably apatite and numerous minute dark inclusions.

As secondary alteration products, hornblende, biotite, iron ore and chlorite are noticed.

The mode of the rock is given below:

Plagioclase	37 6	Chlorite and Amphibole ..	16·9
Micropegmatite	8·3	Magnetite	2·5
Pyroxene	33·5	Biotite .	1·4

The modal feldspar and pyroxene are less than the normative amounts on account of the alteration of these minerals to secondary products.

General Review of Chemical Composition

Having made a petrographical study of the traps we can proceed to review their general chemical characters and compare them with well-known types such as the plateau-basalts and tholeiites from India and elsewhere.

Considering the analyses A to II (Table III) it is seen that type A is distinctly different from the others Its silica content is lowest and alumina is less than in the other rocks The iron-oxides present are about normal to basalts, with ferrous oxide dominating over ferric; magnesia is decidedly high while

TABLE III

Analyses of the Cuddapah Traps

	A	B	C	D	E	F	G	I	II	III
SiO_2 ..	45 23	46 92	48 54	48 95	49 91	50·47	52·02	46 63	50·04	49·20
Al_2O_3 .	8·64	15·93	14·05	15 09	18 06	12·91	15·18	13·26	13·26	14·59
Fe_2O_3..	1·37	3 82	2 94	5 57	1 19	5·61	2 22	3·84	2·94	3·50
FeO ..	11·10	9·28	11·75	7 69	6·42	9·62	8 32	10·94	12 57	9·57
MnO ..	0·26	0·30	0·34	0·24	0·24	0·27	0·25	0·70	0·83	0·40
MgO ..	21 84	6·85	6 43	6 90	7 90	4·88	5·96	6·46	5·22	6 33
CaO ..	6 11	9·73	9·52	5 72	11 24	8 04	11·11	12·20	8·08	9·45
Na_2O ..	1 98	2·66	2 23	3 69	1 93	3 05	2·46	2 73	2·39	2 64
K_2O ..	0·30	0·26	0·69	0 74	0 66	1·13	0·59	0·16	0·72	0 68
TiO_2 ..	0·44	1 82	1·50	1 09	0·60	1 61	0·73	1 60	1·73	1·34
P_2O_5	0 26	0 23	0·14	0·17	0 27	0 19	0·19	0·19	Trace	0 17
H_2O+	2·80	1·93	1·79	3·25	1 48	2·25	1·17	2 81	1 96	2·08
H_2O-	0·25	0·34	0·43	0·57	0·51	0 44	0·29	0 24	0 31	0·39
	99 73	100 17	100 25	100·03*	100 46	100 47	100·49	100 76	100·93	100·29
Sp. Gr	2·803	3 939	3 044	3 913	2 983	2 949	2·994	3·137	3·075	3·004
Temp C	29 5°	29·5°	29·0°	29·5°	29 2°	29 5°	30·75°	.	..	..
					Basis					
Cp ..	0·55	0·29	0 29	0 29	0·56	0 29	0 28	0·39	..	0·29
Kp ..	1·00	1 38	2·46	2 43	2·41	4 21	2·04	0·70	2·47	2·08
Ne ..	5·96	14·85	12·16	20·87	10 44	17·20	13 61	15 33	13·74	14·89
Cal ..	10·47	18·82	16 66	14·09	23·36	11 41	17 53	13 07	14·80	16·27
Cs ..	3 33	5·26	6·17	0 87	4 63	6·58	7·91	12·20	5·29	6·23
Fs ..	1 50	4·14	3·13	6 09	1·35	6 15	2·38	4 18	3·17	3·81
Fa ..	13·13	11·48	14·59	9·57	7 75	12·03	10 13	14·03	16 38	12·02
Fo .	45·37	14 76	13·98	15·04	16·76	10·71	12·66	14 12	11 45	13·66
Ru ..	0·29	1 32	1·10	0·81	0·45	1·17	0 51	1·16	1·23	0·98
Q ..	18 39	27·70	29·47	29 01	32 29	30 25	32·98	24·92	31·47	29·75
	100 00	100·00	100·00	100 00†	100·00	100 00	100 00	100·00	100·00	100 00
					Kala Norm					
Q ..	..	..	..	..		2·69	2 15	..	1·93	..
Or ..	1·67	2·30	4 05	4·05	4 02	7·02	3·40	1 17	4·12	3·47
Ab ..	9 97	24·75	20·27	34 78	17·40	28·67	22·68	25·55	23·90	24·82
An ..	17·45	31·37	27·80	23 48	38 93	19·02	29·22	21 78	24·67	27·12
Wo ..	3·88	4·37	6·03	1·16	5·27	6·43	9·53	13·98	4·59	6·35
Hy ..	5 88	7·24	15 60	8·24	8·88	11 94	11·92	6·44	19·73	12·74
En ..	19·68	11·38	16·90	19·16	20·24	14·28	16·91	7·60	15 90	16 88
Fa ..	7·97	3·98	1 33	0·35	0·42	.	.	7·11	..	0·56
Fo ..	30·61	6·24	1·20	0·66	1·58	..	..	8 42	..	1·02
Tn ..	0·84	3·96	3·30	..	1·35	3·51	1·53	3·48	3 69	2·94
Mt ..	1·50	4·14	3·13	6·09	1·35	6·15	2·38	4·18	3·17	3·81
Ap ..	0·55	0·29	0·29	0·29	0 56	0·29	0·28	0·29	..	0·29
	100·00	100·00	100·00	100·00‡	100·00	100·00	100·00	100·00	100·00	100·00

TABLE III—*Contd*

	A	B	C	D	E	F	G	I	II	III
					C I P W Norm					
Q ..	..	..	0 24	0 48	..	3 96	2 82	..	3·18	0 54
Or .	1·67	2 22	3·89	3·89	3 89	6·67	3 34	1·11	3 89	3·34
Ab ..	9 43	22 53	18 34	31 44	16·24	25 68	20·90	23 06	20 44	22 53
An .	17 51	30 30	20 69	22 52	38 64	18 07	28 62	20 85	23 35	26·13
Di .	8 90	13 82	16 36	2·26	13 36	17 16	21 24	32 13	13·96	16 45
Hy	20·91	13·74	25 27	24 26	23·09	14·56	17·12	0·33	25·38	20 90
Ol	34·82	5 81	..	.	0 62	..	..	11 34	.	.
Il ..	0·76	3 50	2 89	2 13	1·22	3 04	1 37	3 04	3 19	2·58
Mt .	2·09	5·57	4·18	8·12	1·86	8·12	3 25	5 57	4·18	5·10
Ap ..	0·67	0 34	0·34	0·34	0 67	0 34	0 34	0·34	..	0·34
H_2O .	3·06	2·27	2·22	3 82	1·99	2·69	1·46	3·06	2 27	2·47
	99·81	100·10	100·42	100 06‡	100 58	100 29	100·53	100 82	99 86	100·28

* Total includes 0·36 CO_2 † Total includes 0·93 Cc

‡ Total includes 0 93 Cc and 0·81 Ru § Total includes 0·80 of $CaCO_3$.

A *Picrite* (No. 5) From the middle of the composite sill near 35 miles 2½ furlongs on the Cuddapah-Pulivendla road Analyst N A. Vemban

B. *Pyroxene dolerite* (No 30) 1303 Beduduru Hill (Sheet 57 J/1) Analyst N A Vemban

C. *Dolerite* (No 9) From near the village Vemula on the Cuddapah-Pulivendla road. Analyst N A Vemban

D. *Vesicular basalt—Porphry* (No 46) 7th mile on the road from Betamcherla to Kalwa Analyst N A Vemban

E *Quartz-dolerite* (No 4) : From upper portion of the still, 35 miles 2½ furlongs on the Cuddapah-Pulivendla road, Analyst N. A Vemban.

F *Fine-grained basalt* (No 49) Eastern end of Brahmanapalle asbestos zone, Pulivendla taluk, Cuddapah district Analyst N. A Vemban

G *Quartz-dolerite* (No 2*b*) · From the hillock west of Tiruttam, Chittoor district Analyst N A. Vemban.

I *Dolerite* below asbestos zone, Brahmanapalle asbestos mine, Pulivendla taluk, Cuddapah district, *Mem G.S I.*, 64, p. 224, 1934 Analysts P C Roy and Mahadeo Ram.

II *Quartz-dolerite* below asbestos zone, a quarter of a mile south-west of Malkapuram, Dhone taluk, Kurnool district. *Ibid*

III. Average of 8 analyses of Cuddapah traps B to II

CaO, alkalis and titania are low This rock comes under the peridotite-picrite group.

The most striking feature in the series of analyses is the uniformity in composition of the dolerites and basalts with the silica percentage varying from 46·92 to 52·02 per cent. Alumina is present in about the usual amount expected in basalts, except in E which is highly feldspathic. The iron oxides

are usually high except in E and G. Ferrous oxide predominates over the ferric in general but the high ferric oxide content in D and F can be accounted for by the considerable amount of palagonite present. Manganese is low. Compared to the combined iron oxides the amount of MgO is lower The CaO is about normal Soda dominates over potash, but in D and F soda is notably higher Titanium and phosphorus are both in about the normal amounts.

A comparison of the mean analysis of the Cuddapah traps (Table IV) with the average Deccan traps shows that they are closely akin to each other. There is also a close resemblance between the 'Newer dolerites' of Bihar and Orissa and the Cuddapah traps. In comparison, the Gwalior trap contains less alumina and more alkalis The average analyses of the Karroo dolerites, the Whin Sill and the New Jersey basalts compare closely with that of the Cuddapah traps, as all of them come under the normal tholeiitic types.

Petrochemistry

For the present study seven analyses of Cuddapah traps were made by the writer and two previous published analyses have been added. This form of expressing the composition (weight percentage of the chief oxides) is not by itself quite suitable for petrographic classification and comparison or for understanding the chemical characters of the rocks and their evolution. For such a study, various new values were calculated by grouping together allied oxides having the molecular proportions of the various oxides as the basis of calculations according to the method of Niggli, which is very helpful in the study of differentiation and of magmatic affinities of rocks. The various calculated values are given in Table V.

Differentiation Trends in the Cuddapah Traps

The rock types under study are all basic in character with the silica content varying from 45 to 52 per cent. (by weight). This small range in silica percentage goes to show that the magma that gave rise to the various types did not undergo extensive differentiation and that most of the rocks represent more or less the composition of the magma itself. Though the silica expressed as weight percentage has a very small range, we can see from the Niggli values that 'si' varies from 81 to 128 units and that there is a well-marked gap of 22 units between si 81 and 103; but there is every gradation from si 103 to 128. This gap is significant for study of the nature and evolution of this magma. In Fig. 3 a generalised differentiation diagram has been drawn from the Niggli values with *si* as abscissa and the other

TABLE IV

Average Analyses of the Cuddapah Traps and other basic rocks compared with them

	I	II	III	IV	V	VI	VII	VIII
SiO_2 ..	49 20	50·61	52 11	50 18	50·59	52·25	50 66	48 76
Al_2O_3 .	14·59	13·58	14·35	11·73	13 76	14 60	14·28	15·85
Fe_2O_3 .	3·50	3 19	1·38	3·02	3·87	0·84	3·41	5·37
FeO ..	9·57	9·92	9·94	11 94	8 50	9 89	8 58	6 34
MnO .	0·40	0 16	0·18	0·50	0·16	0·45	0·12	0·39
MgO ..	6·33	5·46	5·73	5·45	5·42	6·95	6·92	6·03
CaO ..	9·48	9·45	8·85	10·05	9·09	9·71	8 69	8·91
Na_2O ..	2·64	2 60	2·97	4·47	2 42	2·21	2 92	3·13
K_2O .	0·68	0·72	1·15	0·95	0·96	0·96	0 72	1·68
TiO_2 ..	1 34	1·91	0 80	1·59	2·39	1 10	1·30	1·39
P_2O_5 ..	0·17	0·39	0·24	0 74	0·26	0·22	0·17	0·47
H_2O+ .	2·06	1 70	2·06	0 81	1·51	0 71	2·28	1·76
H_2O- .	0 39	0·43	0·17		0·76	0·32		
	100·39	100 12	99 95	100·43	100 21*	100·21	99·96	100 99
Sp Gr	9 004	2·916		2·98	..	2 990	..	.
si .	116·8	126 2	131 1	117·6	129·1	126·1	123 6	117·0
al ..	20·4	20·0	21·3	16·2	20·7	20·7	20·5	22·4
fm ..	48·6	47·3	45·6	47 0	46·6	47·6	49 0	44·7
c .	24·1	25 3	23 8	25·2	25 0	25 0	22·5	22·9
alk ..	6·9	7 4	9·3	11·6	7·7	6·7	8·0	10·0
ti .	2·4	3·6	1·5	2·8	4·6	2·0	2·3	2·6
p ..	0·14	0·42	0·15	0·73	0 31	0 14	0·15	0·58
k	0·12	0·15	0·23	0·12	0·22	0·24	0·13	0·35
mg ..	0·46	0·43	0·47	0·41	0·45	0·53	0·52	0·50

* Total includes 0 58 CO_2 and 0 11 Incl

I. *c*-gabbroid
II *c*-gabbroid
III. Normalgabbrodioritisch
IV. Normalgabbrotheralithisch
V *c*-gabbroid
VI. *c*-gabbroid
VII Normalgabbroid
Normalgabbrodioritisch
VIII Normalgabbrodioritisch

I. Average of 8 analyses of Cuddapah traps B to H given in Table III.

II *Deccan Trap* — Average of 11 analyses including 1 Rajmahal trap *Bull Geol Soc. America*, Vol 33, p. 774, 1922. Analyst H S. Washington

III. *Newer dolerite* — Bihar and Orissa Average of 3 of Singhbhum *Rec., G.S.I.*, LXV, p 528, 1932 and 2 of Keonjhar State, *Rec., G.S I.*, Vol. 71, p 108, 1936. Analysts L. A N Iyer and P C. Roy

IV *Gwalior trap* — Average of 6 analyses *Jour. Geol*, XLIII, p. 69, 1935. Analyst M P. Bajpai

V. *White Sill:* — Average of 6 analyses. *Min. Mag.*, XXI, p. 539, 1928. Analyst H F. Harwood.

VI. *Karroo dolerite* — Average of 5 analyses. *Geol. Mag.*, LXVII, p. 101, 1930. Analysts E G. Radley and Prior.

VII. *Average New Jersey basalt:* — Quoted from C. A. Anderson. *Amer Jour. Sci.*, 238, p. 486, 1940.

VIII *Daly's average basalt* — Quoted from Washington, *Bull. Geol. Soc. America*,

TABLE V

Niggli, QLM and πγ values of the Cuddapah Traps

	A	B	C	D	E	F	G	I	II
si	80 7	107 4	113 4	121·8	115 2	127·6	125·7	102·8	124 1
al	9·0	21·4	19·3	22·1	24 5	19·1	21·0	16·0	19·4
fm	77 1	48·3	51·0	52·7	42·5	49·9	42·9	49·1	52·4
c	11 7	23·8	23·8	15·2	27·7	21·7	28 8	28 8	21·4
alk	2·2	6·5	5·9	10·0	5·3	9·3	6·7	6 1	6·8
ti	0·53	2·2	2·7	2 1	1·1	3·0	1·3	2 7	3·1
p	0·21	0·14	0·14	0·15	0 28	0·16	0·14	0·13	.
k	0·14	0·09	0·17	0·10	0·18	0·20	0 13	0·04	0·15
mg	0·76	0·49	0·44	0·49	0·65	0·37	0·50	0·44	0·37
Q	18·8	28·5	30·2	29 9	32·5	31·0	33 3	25 6	32·1
L	17·5	35·0	31·3	37·7	26 2	32·8	33 2	29 1	31 0
M	63·7	36·5	38·5	32·4	31·0	36·2	33·6	45·3	36·9
n	0·68	0·54	0·53	0 38	0 65	0·25	0·53	0·45	0·48
γ	0·05	0·15	0·16	0·03	0·15	0·19	0·24	0·27	0·15

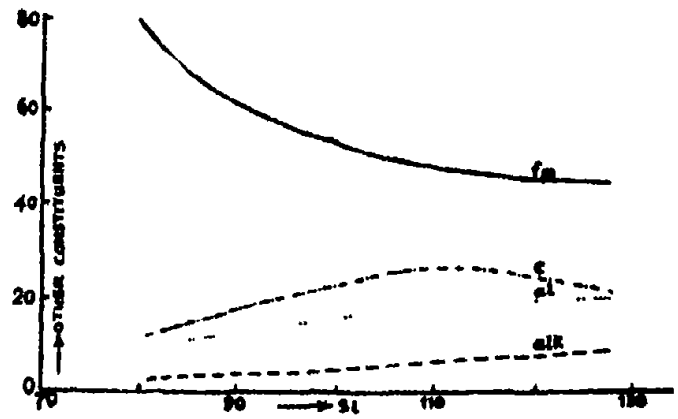


FIG. 3 Differentiation diagram of the Cuddapah Traps

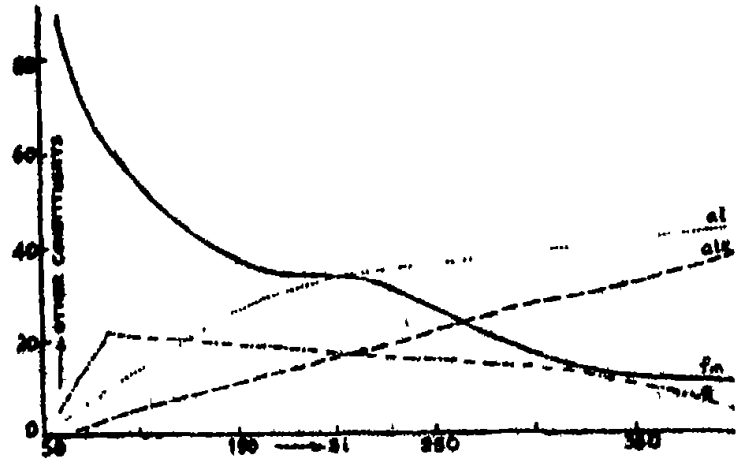


FIG. 3a. Differentiation diagram of the calc-alkali series (After Niggli)

constituents as ordinate. There are three curves which are roughly mutually sympathetic, but antipathetic to the *fm* curve. The curve *c* rises more rapidly than the *al* curve but it becomes sympathetic to *fm* curve at about *si* 112. The *alk* curve, on the other hand, rises only very gently. The *fm* curve is steep from *si* 81 to 110, the value of *fm* changing rapidly for a small variation in *si*, but it becomes flatter afterwards.

The Niggli differentiation diagram does not give us an idea of the individual behaviour of soda and potash, or of magnesia which are grouped together in the *alk* and *fm* values To study this, the values *k* and *mg* can be plotted, with *k* as abscissa and *mg* as ordinate The relationship between these two components during the progress of differentiation can be understood from Fig. 4. It is seen that there is comparatively little variation in *k*,

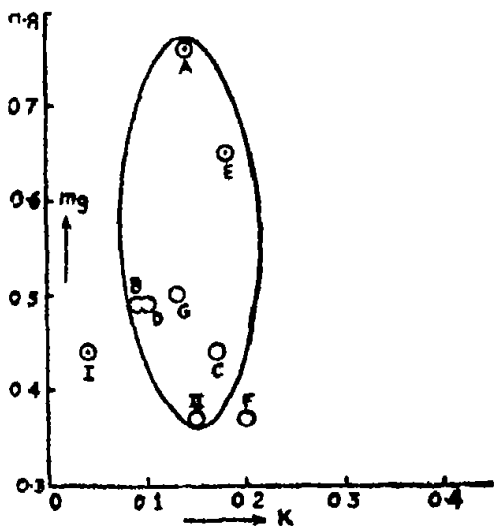


FIG 4

k – *mg* diagram for the Cuddapah Traps

the maximum being 0·16, while the *mg* values have a range of as much as 0·39. The points occupy a small linear zone which is nearly vertical in position to the abscissa, this being found commonly in potash suites The reciprocal relationship which is characteristic of calc-alkaline suite is not clearly seen in the diagram.

The normative mineral composition of a rock can be estimated from its Niggli values. When there is enough silica and when *al* is less than the sum (*alk* + *c*), the value 2 *alk* gives the proportion of the alkali-feldspars, 2 (*al* – *alk*) that of the anorthite content, and (100 – 2 *al*) that of the melanocratic (ferromagnesian) minerals. The sum of these three values is

always equal to 100 and can be represented by a single point in a trilinear co-ordinate diagram in which the three corners represent 100 per cent. of the three values.

When these values are plotted on a trilinear co-ordinate diagram (Fig. 5), a clear idea is gained of the basicity of the rocks and also of the general trend

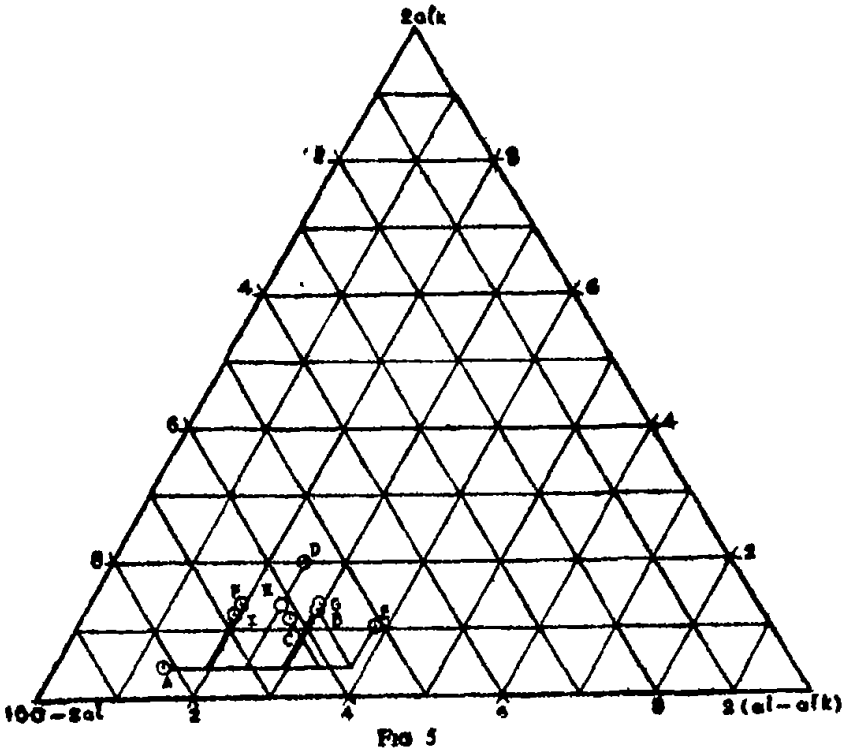


Fig 5

2 *alk* − 100 — 2 *al* − 2 (*al* − *alk*) diagram for the Cuddapah Traps

of consolidation of the magma, which conforms to the theory of crystallisation-differentiation, *viz.*, the progressive enrichment in alkali feldspar.

From the diagram the magma can be regarded as having followed three different lines of development during the evolution of the various types.

1. The impoverishment in ferromagnesians with constant alkali-feldspars.
2. The enrichment in alkali-feldspars with constant dark minerals.
3. The enrichment in alkali-feldspars with constant anorthite content.

From the point A the first trend operated and, during the progress of this, the second and third courses have given rise to the other types. We cannot say definitely which type is the result of these two differentiation

tendencies as the points can be joined either way, but we can regard the types E and D as resulting from the enrichment of alkali-feldspars with constant anorthite content Of these two, the type D has higher alkali-feldspars while E is richer in anorthite content

The QLM-Diagram

The *QLM*-diagram is very important in tracing the magmatic affinities of the rocks and the sequence of formation of the various types and also the order of crystallisation of the minerals composing the rocks As the role of quartz is important in the formation of different rocks, the behaviour of quartz in the differentiation history can very well be followed in this diagram

When the *QLM* values (Table V) of the Cuddapah magma types are plotted in the diagram (Fig. 6) prepared by Niggli (1938, Figs. 2*a*, 20 and 21), it is seen that all the points except A fall below the line PF (saturation line) and above PL in the area of ' Normal basalt ' within the main basalt field The point A, representing a peridotitic type falls outside the above field All the so-called ' primary basalts ' of all parts of the world (such as tholeiite, ophiolith, norite, plateau-basalt and olivine-basalt) fall within the borders of ' Normal basalt '.

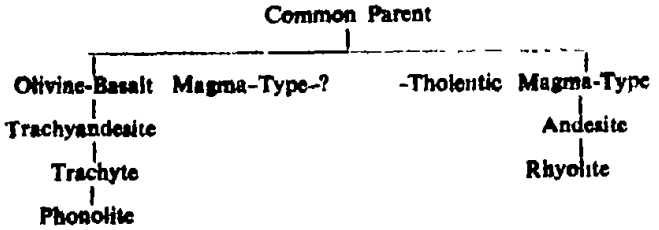
Most petrologists now regard all igneous rocks as derived generally from a basaltic magma, though such a magma may not necessarily be considered the starting point in all cases In this connection Bowen has written (p. 5, 1928)

> " To Daly, in particular, we owe the demonstration, apparently satisfactory, that basaltic magma is a constant member of all these associations and that there is no essential difference in the basaltic magma of the various associations. Partly for this reason and partly on geologic grounds he considers that basaltic magma is the parental magma of all igneous-rock series, except certain pre-Cambrian rocks. The facts are not such as to enforce belief in the parental nature of basaltic magma but they are sufficiently definite that many petrologists now entertain the belief favourably and include it in their general scheme of rock derivation In the present discussion the parental nature of basaltic magma is taken as a fundamental thesis and other rock-types are developed principally by fractional crystallisation..... The reasons for preferring a thoroughly basic, presumably basaltic, parental magma are, however, strong and will become apparent as the discussion proceeds."

Thus Bowen derives the various rock types from basic and basaltic magma, supported by his experiments on liquid melts in the laboratory.

To him crystal fractionation is the chief cause of the diversity of rocks. He believes that basaltic magma generally gives rise to quartzose late differentiates but under certain conditions a liquid deficient in silica may be filter-pressed before reaction with early-formed crystals such as pyroxenes; or the liquid may be rich in silica if filter-pressed during peritectic reaction, leaving behind feldspathoids. Daly, on the other hand, considers that 'primary basalt' magma is capable of giving rise to various rock-types but he attributes the formation of alkaline rocks primarily to the desilication of basaltic magma by wide-spread assimilation of limestones and calcareous sediments Thus both the authorities view the alkaline rocks as abnormal and derived under exceptional circumstances from the 'primary basaltic' magma. Contrary to the views of Bowen and Daly, W Q Kennedy (p. 256, 1933) basing his conclusions on the investigations of the authors of the Mull Memoir, says:

> "Study of individual rock bodies and regional magmatic provinces leads to the conclusion that there exist two great primary basalt magmas, the olivine-basalt type and the tholeiitic basalt type, each of which gives rise normally to its own particular line of descent. The former is the parent of the alkaline rock suite and the latter is the parent of the calc-alkaline suite as follows:



> There is no evidence that either of these "primary" magmas is a derivative of the other nor can we point to any common parent from which they could have been derived... ." "Any such relationship is too far removed from the scope of the present investigation to merit discussion, and all that seems certain is that both types of basaltic magma have been available throughout geological history in immense amounts and over immense areas. We are justified, therefore, in regarding them, for the purposes of petrogenesis, as primary magmas."

Thus Kennedy maintains that a particular late differentiate is determined only by the nature of the primary magma and is not the result of the physico-chemical conditions obtained during solidification.

Niggli (1938) prefers to assume two or even a larger (yet limited) number of well-defined basaltic 'Stammagmas' ("Zwei oder einer kleinen Zahl

wohldefinierter basaltischer Stammagmen," p 653, 1938) for the derivation of rock-types of petrographic provinces. Niggli uses the terms 'Ausgangs' or 'Stammagma' instead of 'primary magma' since there is a great variation in the composition of the basic magma, as is shown by the large basaltic field in the *QLM*-diagram (Fig. 6)

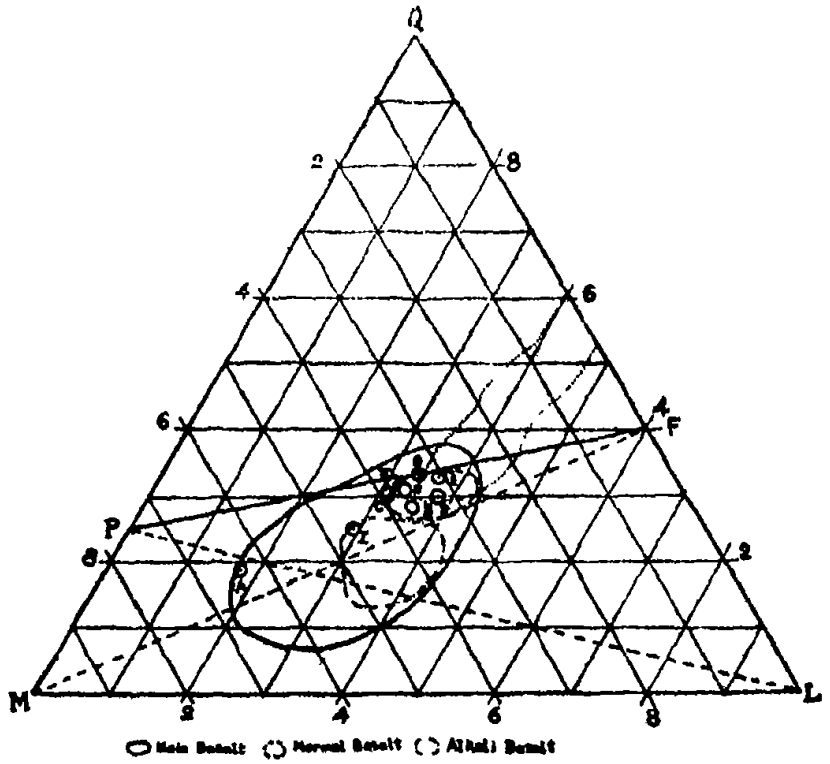


FIG. 6
QLM – Diagram of the Cuddapah Traps

Basing his observations on his molecular values, Niggli has found that the olivine-basalt or 'plateau-basalt' type is essentially of normalgabbroid to hornblenditisch and that the tholeiitic type varies from normalgabbrodioritisch to miharaitisch. He says that the theory of Kennedy holds often, but on a careful investigation one can observe all possible intermediate members in between these two types; as the chemical difference itself is relatively small, so that normalgabbroid types are found also in typical Pacific provinces and gabbrodioritisch in the Atlantic. On a comparison of the molecular values of tholeiite and norite and of 'plateau-basalts' and tholeiites, and from the association of hornblenditisch and hornblendeperidotitisch

types with 'plateau-basalts' and tholeiites, he concludes that tholeiite was derived from completely fluid magmas of hornblenditisch and hornblende-peridotitisch composition and that, as these magmas give rise to heteromorphous rock-types with such monomineralic rocks as amphibole picrite and hornblendite which exhibit similar composition included in them, the further course of differentiation depends entirely upon the predetermined primary molecular constitution of the early formed crystals combined with the trend of diffusion.

H Kuno (1937), after a chemical study of many basalts, quite different from that of Niggli, arrived at a similar conclusion (p. 208), namely, that "these rocks are differentiates of more basic magmas by fractional crystallisation" and that "the ultimate primary magma from which these rocks have been derived are supposed to have had the composition of an olivine-rich eucrite" He expressed the general trend of differentiation of this primary eucrite magma in the following tentative scheme:

Primary Olivine-eucrite magma

Olivine-basalt Magma-type

Mugearites, Trachyandesite, etc

Trachytes and other acid alkaline rocks

(Saturated Olivine-basalts, such as those of Hawaii and Iceland)

Tholeiitic Magma-Type

Pyroxene-andesites

Rhyolites

Even though there is agreement between Niggli and Kuno in considering the plateau-basalts as derivatives from a more basic magma, Niggli conceives of a magma of ultrabasic composition while the 'primary magma' of Kuno is gabbroidal or noritic This latter according to Niggli is derived from a more basic magma; but the attractiveness of Kuno's theory lies in considering the tholeiite type as the derivative of olivine-basalt which is an amplification of the observations of Niggli

In conceiving of the plateau and olivine-basalt magmas as derived from liquid ultra-mafics, we have to face the objection raised by Bowen. Bowen (1927 and 1928) denies the existence of peridotitic magma and concludes that monomineralic rocks such as dunite, anorthosite, etc, do not represent the composition of the magma from which they were formed but are accumulations of early-formed crystals which separated from the liquid by crystal fractionation. He supports his view by experimental work on liquid melts which indicates that ultra-mafic magmas can be liquid only at prohibitively high temperatures. But C. N. Fenner (1938) and H H. Hess (1938) consider

that hyperfusible constituents would have a controlling effect on the temperature. C. N Fenner states (p. 399, 1938)·

> "This leads to the conclusion that, contrary to inferences reached in the theory of crystal fractionation, wholly liquid magmas of ultrabasic composition exist."

The views of Fenner and Hess may perhaps be verified in a few localities, but it may not follow that all peridotites represent direct product of solidification from the magma of the same composition On the other hand, Bowen has clearly shown that certain peridotites are the result of accumulations of early-formed crystals from a basaltic or noritic magma In the case of the peridotites of Skye he pointed out that the chilled marginal facies of the ultra-mafics carried phenocrysts of olivine in a fine-grained basaltic matrix, indicating that the core is the result of accumulations of early crystals from which the residual liquid was filter-pressed. We should, therefore, look for positive proof in the field regarding the origin of such types as the trap from which the (analysed) specimen A was collected. In this connection it may be worth noting that C S. Fox (quoted by A. L Coulson, p 150, 1934) describing the occurrence and field relations of this trap, states

> "The ridge (west of Pulivendla Inspection Bungalow) appears to consist of a composite sill (three separate sills) of dolerite, the middle one, a dark, coarse, scoriaceous-weathering rock being rich in olivine, while the layers above and below it are dolerites without olivine"

A L Coulson comments thus on the statement of Fox.

> "These observations of Dr Fox have great interest and deserve amplification The author collected specimens of the sill which bear out Dr. Fox's remarks Thus the uppermost part of the sill is best described as a quartz-dolerite It is very similar to a specimen of what is undoubtedly the same sill collected near the 38th milepost on the Cuddapah-Pulivendla road, 1¼ miles WNW of Vemula."
>
> "The central portion of the sill is very basic and contains abundant augite, olivine, (?) hypersthene, serpentine, a little feldspar, iron-ore and brown mica. It is a picrite It also has its counterpart in a similar specimen collected near Vemula.
>
> The lowest portion of the compound sill is intermediate in basicity between the uppermost and central parts, being best described as a dolerite."

From his own field and laboratory studies the present writer is quite in agreement with the above description. The upper and lower dolerites do

not appear to be the border facies formed as the result of filter pressing of the residual liquid, nor do they contain any olivine phenocrysts to warrant such an assumption; but they do represent quite separate phases of intrusion. It is suggested, therefore, that type A represents the primary magma of the composition of picrite from which other types were possibly differentiated.

In Fig. 6 is shown the main basalt field in which are distinguished ' Normal basalt ' and ' alkali basalt ' and a well marked area of calc-alkaline rocks. It can be seen that the major portion of the ' Normal basalt ' represented by tholeiite, ophiolith and ' plateau-basalt ' is occupied by calc-alkaline field. When the *QLM* values of the Cuddapah traps are plotted, it is seen that all the normal types occupy the region of ' Normal basalt ' while A and I which are distinctly earlier in the differentiation series are found towards the side M. There is only one trend of differentiation, from picritic composition towards the calc-alkaline field as shown below

Picrite (hornblendeperidotitisch)
(*si*-pyroxenitisch
dolerites normalgabbroid or *c*-gabbroid)
quartz dolerites (normalgabbrodioritisch or miharaitisch)

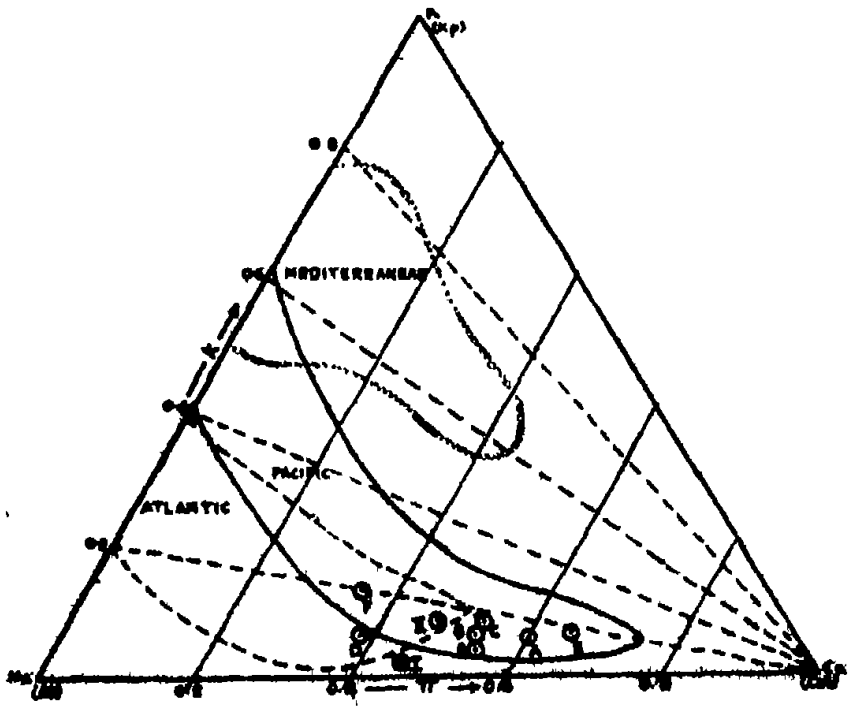


FIG. 7

k_w Diagram for

The k-π-Diagram

The same trend of differentiation is also indicated when we study the interrelation between the three Basis molecules Kp, Ne and Cal, which is brought about by k and π values themselves, on a triangular diagram whose corners are Kp, Ne and Cal, in which the three generalised diagrams constructed by Niggli (Figs. 2*b*, 3*b* and 4*b*, 1938) for the three petrographic suites are included in a simplified form. When k and π values for the Cuddapah traps are plotted in the diagram (Fig. 7) it is seen that except for the points D and I all the others fall within the field of the Pacific suite.

It is evident from these studies that the Cuddapah intrusive belongs to the calc-alkaline suite.

Summary and Conclusion

The traps of Cuddapah age mark an important period of volcanic activity later in age than the Dharwars and probably earlier than the Cambrian The chief character that distinguishes the Cuddapah traps from those of Dharwar age is the marked freedom of the former from metamorphism as the Peninsula was free from major earth movements after their intrusion

In the present work an attempt is made to study the petrography and petrochemistry of these basic rocks collected from several sills intrusive into the Vempalle limestones and the Tadpatri shales in the Ceded districts

These trap rocks are composed of colourless, non-pleochroic pyroxenes and labradorite feldspars with sub-ophitic to doleritic textural relationship between these two minerals indicating that they crystallised more or less simultaneously This is also confirmed by the f(norm) values. The pyroxenes belong mostly to the monoclinic variety, augite, the other monoclinic pyroxene, pigeonite being rare or absent; in the olivine-bearing types there is also the rhombic pyroxene, enstatite. The optic axial angle of the augite varies from 56° to 40° and the extinction angle from 46° to 36° The enstatite is optically negative ($2V = -83° \pm 2°$) and is rich in magnesium

The Cuddapah traps, the Newer dolerites and the Gwalior traps are similar to each other in their pyroxenes being mainly augite with a large optic axial angle. They differ from the Deccan traps, the Karroo dolerites, the Whin Sill and the New Jersey diabases in the absence of pigeonite which characterises those rocks. The average composition of the plagioclase, deduced from both Universal Stage determinations and chemical analyses is found to range from bytownite with 75 per cent. anorthite to oligoclase or andesine of 30 per cent. anorthite with a mean value of about 55 per cent. anorthite.

From a study of the analyses, six distinct magma-types (Niggli's) have been recognised:

1. Melagabbrodioritisch
2. Miharaitisch
3. Normalgabbroid
4. *c*-gabbroid
5. *si*-pyroxenitisch
6. Hornblendeperidotitisch.

Petrochemical studies, using Prof. Niggli's methods, show that the rocks are basaltic in nature with only a limited range of differentiation. The differentiation diagram based on the Niggli molecular values, *QLM* values and *km* values show that the Cuddapah magma belongs to the 'Normal basalt' of Niggli (= Tholeiite type) and that the trend of differentiation is similar to that of the calc-alkaline suite of rocks

These conclusions are only of a limited validity as the number of specimens analysed is small. As these traps occur extensively and over large areas, there is scope for the extensive collection and study of much material which will lead to a wider understanding of the nature and history of these rocks

ACKNOWLEDGEMENTS

In conclusion, I wish to express my gratefulness to Prof T N. Muthuswami, Professor of Geology, Presidency College, Madras, for guidance during the whole course of this work and for giving me all facilities for laboratory work. I am indebted to Mr M S. Balasundaram, Assistant Geologist, Geological Survey of India, for affording me an opportunity of studying some of his collections of Cuddapah traps from the Ceded districts for purposes of comparison Lastly, I wish to place on record my sincere thanks to Dr. M S Krishnan of the Geological Survey of India for many useful and instructive suggestions in the presentation of the results of this study.

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CHEMICAL EXAMINATION OF THE FRUITS OF *TERMINALIA BELERICA* ROXB.

Part II. The Component Glycerides of the Fatty Oil

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[THE component glycerides of the seed oil of *Terminalia belerica* have been examined. The amounts of oleic, linoleic, palmitic and stearic acids have been found to be in fair agreement with those reported[1] in Part I. The component glycerides of the oil are Palmitooleolinolein 35·24%, Stearooleolinolein 43·51%, Palmitodiolein 1·07%, Stearodiolein 1·95%, Dioleolinolein 9·54% and Triolein 8·69%.]

In a previous communication,[1] the percentage composition of the component fatty acids of the oil from the kernels of the fruit of *Terminalia belerica* (natural order *Combretaceæ*) has been reported by Saran and Singh; the present work is in continuation of it and deals with the glyceride structure of the oil. A few other species of *Terminalia* have also been examined for the composition of seed oil, namely, *T. catappa* from East Indies[2] and West Africa[3] and *T. chebula*.[4] The major component acids of these oils are oleic, linoleic and palmitic, stearic acid being present in only minor proportions. The fatty acid composition of *T. belerica* as found directly by Saran and Singh is in fair agreement with that determined from the glyceride composition of the oil as shown below:

	Oleic	Linoleic	Palmitic	Stearic
Saran and Singh (direct determination)	43·21%	28·99%	11·80%	16·00%
Present authors (glyceride structure)	43·68%	29·56%	11·28%	15·48%

It will be thus seen that oleic and linoleic acids are the major components of all *Terminalia* species, the amount ranging between 56 to 84%. There is, however, this difference that whereas stearic acid is present only in minor proportions and is not a major component in other species of *Terminalia* so far investigated, it becomes a major component (over 15%) along with palmitic acid (over 11%) in the seed oil of *T. belerica*.

The number of glycerides present in the seed oil of *T. belerica* is found to be six, whereas the total number of glycerides which can be formed from four acids and the glyceryl radical, $CH_2-CH-CH_2$, is forty.

Experimental

The oil extracted from the crushed kernels of the fruit of *T. belerica* with petroleum ether (40°–60°) was purified with animal charcoal and Fuller's earth, dried over fused calcium chloride, neutralised with sodium carbonate and filtered.

One hundred grams of the oil was chilled[4-6] in the frigidaire with six times its weight of pure and dry acetone for a week. No solid separated showing the absence of trisaturated and disaturated-monounsaturated glycerides. The experiment was repeated twice with each of the following samples of the oil:—

(*a*) Freshly extracted and purified oil, (*b*) about one year old oil, and (*c*) sample of oil used by Saran and Singh, but in no case any solid glyceride separated. The absence of trisaturated glyceride was further confirmed by oxidising the oil dissolved in pure and dry acetone with powdered potassium permanganate.[7]

One hundred grams of the oil was brominated[4-6] in ten times its weight of dry petroleum ether (40°–60°) at − 5° C. till the brown colour persisted. It was kept in the frigidaire overnight. No solid separated. Excess of bromine was destroyed with sodium thiosulphate solution, washed, dried over fused calcium chloride and the solvent distilled off. The viscous residue was extracted with absolute alcohol, absolute alcohol + acetone (1 : 1), methyl alcohol + acetone (1 : 1) and acetone in succession.

The scheme of separation is given below:—

Neutral Oil (100 gm.) (Brominated in dry petroleum ether)

- Insoluble (nil)
- Soluble (excess of bromine destroyed, washed, dried & solvent distilled off. Extracted with absolute alcohol)
  - Insoluble [extracted with absolute alcohol + acetone (1 : 1)] — Soluble F_1 (26·5 gm.)
  - Insoluble [extracted with methyl alcohol + acetone (1 : 1)] — Soluble F_2 (78·1 gm.)
  - Insoluble (extracted with acetone) — Soluble F_3 (5·9 gm.)
  - Insoluble (nil) — All soluble F_4 (45·4 gm.)

The fractions F_1, F_2, F_3 and F_4 were debrominated by taking them in methyl alcohol, adding zinc dust, saturating with dry hydrogen chloride gas

and heating for several hours under reflux in the water-bath. The brominated products were saponified, the unsaponifiable matter removed and the mixed fatty acids liberated. The quantity of individual acids in each fraction was estimated by determining their saponification equivalent and iodine and thiocyanogen values. The quantities of saturated acids being too small in these fractions for estimating them separately, they were considered as one acid and their mean molecular weight determined on extracting with petroleum ether (40°–60°), the oxidation products of each fraction with alkaline potassium permanganate.[10] The glyceride structure was calculated with these data as given below in Tables I to VI.

TABLE I

	F_1	F_2	F_3	F_4
Weight of Brominated glyceride in grams ..	26·5	78·1	5 9	45 4
,, Unsaponifiable matter in gm. .	·25	·26	002	·011
,, Debrominated glyceride in gm. ..	17·52	49·52	3·72	28·96
,, ,, ,, free from unsaponifiable matter	17·27	49·56	3·72	28·94
Weight % of acid ..	17·36	49·80	3·74	29 10
Mol. % of acids ..	17·24	50·13	3·73	28·90
Iodine value of liberated acids ..	84·98	93·09	97·45	96·58
Thiocyanogen value of liberated acids ..	59·94	64·03	67·84	72·00
Mean molecular weight of ,, ,, ..	276·5	272·7	275 1	276·7
Mean molecular weight of solid acids ..	275·0	270·4	273 9	275·4

TABLE II. *Weight % of acids in different fractions*

	F_1	F_2	F_3	F_4
Linoleic .	27·64	32·07	32·66	26·09
Oleic ..	38 81	38·89	42·51	54·95
Solid ..	33·55	29·04	24·81	19·03

TABLE III. *Weight % of acids on total acids*

	F_1	F_2	F_3	F_4	Mean
	17·36	49·80	3·74	29·10	100
Linoleic ..	4·80	15·96	1·20	7·56	29·56
Oleic ..	6·74	19·36	1·59	15·99	43·68
Solid . ..	5·83	14·48	0·95	5·53	26·76

TABLE IV. *Mol. % of acids in different fractions*

	F_1	F_2	F_3	F_4
Linoleic ..	27 58	21·61	23·58	26·04
Oleic ..	38·39	38·38	42·09	54·64
Solid .	34·03	29 87	25 33	19·36

TABLE V *Mol % of acids on total acids*

	F_1	F_2	F_3	F_4	Mean
Linoleic ..	4·74	15 95	1 21	7 53	29·43
Oleic	6·62	19 21	1·67	15·73	43·18
Solid	5·88	14·97	0 95	5·50	27 30

TABLE VI *Probable glyceride structure*

	F_1	F_2	F_3	F_4	Mean
	17·94	50 13	3·73	28·90	100
1 Trisaturated glyceride .	Nil	Nil	Nil	Nil	
2 Disaturated monounsaturated ..	,,	,,	,,	,,	
3 Monosaturated diunsaturated—					
(*a*) ,, oleolinolein ..	14·22	44·91	2 85	16·77	78·75
(*b*) ,, diolein	3 02	3 02	.	..	3 02
Triunsaturated—					
(*a*) Dioleolinolein ..	..	2·94	0·78	5·82	9·54
(*b*) Triolein	..	2·28	0·10	6·31	8·69

1 By oxidizing the neutral oil dissolved in pure and dry acetone with powdered potassium permanganate.

2. By chilling the neutral oil dissolved in pure and dry acetone at 0° C

3 & 4 By calculating from the component fatty acids of the brominated glyceride in the oil

All the saturated acids have been considered as one acid in the calculation of monosaturated-diunsaturated glycerides. According to the law of even distribution we are justified in assuming that the greater proportion of glycerides exist as monosaturated oleolinolein rather than monosaturated diolein and monosaturated-dilinolein. Further it has been assumed that the solid acids are proportionally divided in different glycerides. From the

above considerations the probable glyceride structure may be given as: Palmitooleolinolein 35·24%, Stearooleolinolein 43 51%; Palmitodiolein 1·07, Stearodiolein 1·95%, Dioleolinolein 9·54% and Triolein 8·69%

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